MGIPC—S1—III-1-93—22-8-45—5,000.

BRITISH CHEMISTS

BRITISH CHEMISTS

Edited by

ALEXANDER FINDLAY

and

WILLIAM HOBSON MILLS

LONDON

THE CHEMICAL SOCIETY

1947

The Council of the Chemical Society gratefully acknowledges the generosity of Messrs. Richard Clay and Company, Ltd., who have defrayed the cost of this volume as a contribution to the Centenary Fund.

INTRODUCTION

This volume, published by the Chemical Society on the occasion of its Centenary, contains memoirs of some of the more distinguished British chemists who have died since the outbreak of the First World War, and the record of their work serves to illustrate the contributions to the advancement of chemistry which have been made by Fellows of the Society during the second half-century of its existence.

Some of the memoirs have been written specially for this volume; others have been reprinted unchanged, or with greater or less modification, from Obituary Notices in the Society's Journal. The account of the life and work of W. H. Perkin, jun., is an abstract of the Memorial Volume published by the Society in 1932. Grateful acknowledgment is made of permission granted by the Council of the Royal Society to reproduce from *Obituary Notices of Fellows of the Royal Society* the memoirs on A. G. Green and A. Lapworth. The memoirs have been arranged in the order of the dates of birth of the men whose life and work they commemorate.

These men form a goodly company and their names are known wherever the study of chemistry is seriously pursued. Sir William Crookes, with whom the series begins, was already a boy of nine when the Society was founded. His discovery of thallium in 1861 was one of the earliest fruits of spectrum analysis, and his pioneering work on electrical discharges in high vacua played a considerable part in preparing the way for the new physics, for it led in a direct line to the discovery of *X*-rays and to the investigations which resulted in the discovery of the electron. His discovery of uranium-X and his invention of the spinthariscope also helped to advance the study of radioactive phenomena.

Sir James Dewar, engaging, like Faraday his great predecessor at the Royal Institution, in the study of the liquefaction of gases, endowed laboratory technique with the charcoal vacuum and facilitated the investigation of the properties of matter at low

temperatures by his invention of the vacuum flask. By achieving the liquefaction of hydrogen he brought the range of attainable temperatures to within twenty degrees of the absolute zero.

By his share in the discovery of argon and by his discovery and isolation of the rarer inert gases of the atmosphere, Sir William Ramsay added a new group of elements to the periodic system. He thereby filled a gap which, left unclosed, must seriously have impeded the progress of chemical theory. The isolation of helium also advanced the study of radioactivity by making possible the identification of the α-particle with the helium nucleus, and after the element had been obtained in quantity it afforded a means of approaching to within one degree of the absolute zero.

The pioneer work of H. B. Dixon notably advanced our knowledge of the process of combustion of hydrocarbon gases and the properties of the explosive wave in gaseous mixtures.

W. H. Perkin, jun., a master of synthesis, advanced organic chemistry in many directions and with remarkable skill unravelled the molecular structure of natural products of many different types, while his younger brother, A. G. Perkin, greatly extended our knowledge of the vegetable dyes. The chemistry of synthetic dyes was enriched by notable contributions from R. Meldola and A. G. Green, as well as from Sir Gilbert Morgan, to whom also we owe a debt for his advances in the borderland between organic and inorganic chemistry.

H. E. Armstrong not only contributed to the chemistry of the terpenes and added to our knowledge of aromatic substitution and the origin of colour but also by his strong personality influenced the progress of chemistry in many ways. Sir William Pope, A. Lapworth, and T. M. Lowry began their chemical careers in his laboratory and came under his inspiration. Pope by his brilliant work in stereochemistry opened new fields of investigation and greatly advanced the study of molecular configuration, Lapworth with rare insight into the processes of chemical change had a large share in laying the foundations of our present views on the mechanism of organic reactions, and Lowry will be specially remembered for his work on mutarotation and optical rotatory dispersion.

Sir Jocelyn Thorpe's researches embraced a great variety of organic compounds and added especially to our knowledge of polybasic acids, complex alicyclic rings, and tautomeric phenomena.

G. Barger and Sir Arthur Harden both had strong biochemical leanings. To Barger we are indebted for advances in our knowledge of the simpler nitrogenous products of animal metabolism and the vegetable alkaloids—especially the alkaloids of ergot—and to Harden for fundamental investigations on alcoholic fermentation in which he discovered the co-enzyme and brought to light the important role of phosphoric acid derivatives in enzyme actions.

The work of these men of the generation that has just passed away cannot be contemplated without pride by the present Society, nor can their example fail to serve as a stimulus and an inspiration to those that come after them.

CONTENTS

Where two authors are named, the first has written the general account of the life and the second the outline of the scientific work of the subject of the Memoir.

WILLIAM CROOKES

WILLIAM CROOKES

1832—1919

Born in the reign of William IV, William Crookes not only became one of the Great Victorians in science, but attained also, in the present century, a position of scientific leadership and esteem which can be reached only by a few; and by the members of the general community he was regarded, in a somewhat special degree, as the representative of science. Dedicated to no single branch of science, although, through his training and the earning of a livelihood, devoted mainly to chemistry, Crookes was eager to pursue the investigation of natural phenomena from whatever direction they might appear. His keen intellect and never-flagging interest in science, rather than profound knowledge; his extraordinary energy and experimental skill; his flashes of intuition and scientific insight led to discoveries which impressed his fellow-scientists as well as laymen in science, and gained for him the highest academic distinctions and official honours.

During his long and crowded life Crookes found time not only to enrich science by his investigations, but also to engage in various applications of science; but it was mainly in the pursuit of pure science and in investigations "motivated solely by a desire to increase knowledge", that he sought for inner satisfaction and self-realisation. His belief in the importance of such work he expressed in the words: "We have any number of practical men, but *brain-craft* is the master of *hand-craft*. England needs brain-craft. We want men who cultivate chemistry for its own sake without substratum of utilitarianism. Men whose discoveries . . . seemed at the time never likely to be of the slightest use to anybody."

In the bent of his mind towards science Crookes owed nothing, apparently, to heredity. How or through whom his interest in chemistry and in science was first aroused we do not know. It is to be gathered, however, that it developed early, for Crookes has himself recorded: "From my earliest recollections I was always trying experiments and reading any book of science I could find. A little

older and I fitted up a cupboard as a sort of laboratory, and caused much annoyance and trouble in the house by generating smells and destroying furniture." Many a chemist of lesser renown has done as much. At the age of fourteen, when the discovery of gun-cotton was announced by Schönbein, Crookes at once proceeded to make some, with such success that he nearly blew up himself and his young school companions. In his later years it was a great satisfaction to Crookes, who had been regarded in the family as a bit of a fool who would never get on, that his parents, who showed no interest in science and had wished for him a career as an architect, lived long enough to feel proud of the scientific reputation which he made.

Although Crookes, in course of time, gained a position of great eminence in science and was able to command high consulting fees, his earlier years were full of struggle. Only the possession of moderate private means enabled him to maintain his wife and family and to carry out the research work which brought him scientific fame and professional recognition. For many years his practice as an analyst and consultant brought him little return, and at one time he seriously considered moving from London to Manchester in the hope of improving his position. Although, as he complained, there was plenty of work to be done, there were so many eminent professors twice his age and standing that they absorbed it all. He failed also to obtain any public appointment. "Within the last few years", he wrote in 1864, "I have gone heart and soul into three competitions for a prize of £200 or £300 a year; I had a dozen rivals—everyone said I stood by far the best chance, but somehow or other I failed.* I shall not try again."

Crookes remained, therefore, through life a private practitioner of chemistry, an analyst and consultant, a lone research worker in the peace and seclusion of his private laboratory. Owing to his failure to obtain an academic post, for which, perhaps, his character and personality did not altogether fit him, he had no opportunity of building up a "school" of research or of exercising a direct personal influence on the instruction and training of future chemists. While, however, the authority of a professorial Chair was denied to him, Crookes was able to exercise a wider and perhaps more powerful

* One of the appointments for which Crookes was a candidate was the Professorship of Chemistry at the Royal Veterinary College, which became vacant in 1860. In the absence of any prominent teaching experience, Crookes based his claim for appointment on "the high scientific and practical reputation now acquired by the *Chemical News*, of which paper I have been the sole manager and editor since its commencement".

influence on the advancement of science and the diffusion of chemical knowledge from the various editorial and presidential Chairs which he filled.

In the little Yorkshire town of Masboro', Joseph Crookes, son of a local tailor, was born in 1792. A lad evidently of brain and energy, as well as ambition, he came, while still in his 'teens, to London, and entered the service of a tailor in Regent Street; and so prosperous became the tailor's business which he there built up and so remunerative the ground-rents in which he invested his savings that when he died in 1884 he was a rich man. It was at 143 Regent Street, on June 17th, 1832, that William Crookes was born as the eldest child of a family of sixteen which Joseph Crookes had by his second wife, Mary Scott, who came from Aynhoe, Northamptonshire. It was his mother, rather than his father, whom William resembled in feature and disposition, and it may be surmised that he derived some of his chief characteristics from her.

There is little to say concerning William Crookes's early years. Improbable as it may appear, he maintained that he remembered learning to stand and walk; and he claimed to have seen Halley's comet on its appearance in 1835. His school education seems to have been somewhat meagre, and at the age of sixteen he entered the Royal College of Chemistry, which had been founded in 1845 with Hofmann as its first Professor. Here Crookes was able to satisfy his inclinations towards study and experimental work in science, and his progress must have been very successful and rapid. Within a year he gained a scholarship which covered the cost of his training for one year, and in 1850 Hofmann appointed him his Junior Assistant. In the following year he became Senior Assistant.

At that time the training in chemistry at the Royal College extended over two years, the first year being devoted to qualitative analysis and the second to quantitative analysis and preparations associated with some kind of research. As a practical exercise, Crookes had been given by Hofmann, in 1850, the task of separating the selenium from 5 kg. of seleniferous deposits from a sulphuric acid works at Tilkerode in the Harz; and with the selenium so obtained Crookes prepared and analysed potassium selenocyanate (a salt analogous to the sulphocyanide or thiocyanate), which had already been prepared, but not analysed, by Berzelius. From the potassium salt Crookes prepared the hitherto unknown selenocyanates of silver and lead, and determined their composition.

Other selenocyanates were produced by the neutralisation of an aqueous solution of selenocyanic acid, but were not further investigated. Attempts to prepare the selenocyanate of mercury led only to the separation of a double salt with mercurous chloride. This short and simple piece of preparative work, Crookes's first essay in "research", was published in German in Liebig's *Annalen* in 1851, the English version being published in the *Quarterly Journal of the Chemical Society* (1852, **4**, 12).

Crookes retained his position as Assistant at the Royal College of Chemistry until 1854, when he was appointed Superintendent of the Meteorological Department at the Radcliffe Observatory at Oxford. There he devoted himself mainly to improving the photo-meteorographic methods of registration. In the following year he became Lecturer on Chemistry at the Chester Training College. No scope, however, was to be found there for either his teaching or research abilities, and so, on his marriage in 1856, he returned to London and set about the task of earning a livelihood and of carrying out research.

Although Crookes had received his training in science under Hofmann, the subjects to which Hofmann devoted his energies appear to have had little attraction for him. Unlike W. H. Perkin, who also studied at the Royal College of Chemistry, he never seems to have been attracted to organic chemistry, and, indeed, to the end of his life remained practically ignorant of this branch of science. It was, perhaps, mainly by Faraday, whose lectures at the Royal Institution he attended, and by Wheatstone, Professor of Natural Philosophy at King's College, London, that Crookes was inspired; and so, after completing his study of the selenocyanates, his interest turned to investigations of a more physical or physico-chemical character, involving the use of physical apparatus.

Even as early as 1852 Crookes became greatly interested in photography, more especially in its use in scientific investigations. For some years he was actively engaged in the development of the photographic process, and several papers relating to photography and a small "Handbook to the Waxed-Paper Process in Photography" were published between 1853 and 1857. It is not surprising, therefore, that Crookes, on returning to London in 1856, sought to turn his interest in photography into a means of earning a livelihood. After acting for a few months as editor of the *Liverpool Photographic Journal*, he held, for two years, the post of Secretary of the London Photographic Society and Editor of its *Journal*,

thereby inaugurating an editorial career which he followed till his death.

It was during the early years of his career, while striving to make a name for himself in the chemical world, that Crookes conceived the project of bringing out a new chemical journal, under the name of the *Chemical News*. He acquired the copyright and goodwill of the *Chemical Gazette*, which had been founded in 1843, and the first number of the *Chemical News*, "a weekly journal devoted to every branch of Chemical Science, and an advocate of the interests of the Chemist and Chemical Manufacturer", was published on December 10th, 1859. In this Journal, of which Crookes assumed the entire proprietorship in 1861, and of which he was, during the greater part of his life, sole manager and editor, there were published general articles, reports of lectures, and "the details of new discoveries and the results of practical research in this and other countries". Crookes's liberality of spirit made him very tolerant, and, perhaps, not always sufficiently critical of the articles which he published. *Chemical News* not only furnished Crookes with an organ of publication for his own views and researches, but, gaining in time a wide circulation, extended his influence, and made his name familiar in both lay and scientific circles at home and abroad. Of its publicity value Crookes was fully appreciative.*

In 1858 Crookes moved to a house at 20 Mornington Road, near Regent's Park, where he fitted up a chemical laboratory in which he was able to carry out his commercial analyses as well as his research work. As early as 1822 Sir John Herschel had shown that when the coloured light imparted to a flame by salts of sodium and potassium is passed through a prism, a spectrum of bright lines separated by dark spaces is obtained. With this phenomenon Crookes, always eager to seize on any new advance in experimental science, made himself familiar, while still Assistant at the Royal College of Chemistry; and, in fact, he came near to anticipating the explanation of the Fraunhofer lines given by Kirchhoff in 1860. It was the introduction of the spectroscope by Kirchhoff and Bunsen in 1860 which led, in their hands, to the discovery of the new element cæsium in the mineral water of Dürkheim, and of rubidium in the mineral

* Crookes's literary activities were not confined to the editing of and writing articles for *Chemical News* and other Journals; he was the author, also, of a number of books of which the following may be mentioned: "Select Methods in Chemical Analysis"; "Manufacture of Beet-root Sugar in England"; "Handbook of Dyeing and Calico Printing"; Revision of Mitchell's "Manual of Practical Assaying"; "Phenomena of Modern Spiritualism".

lepidolite. It was by the use of the spectroscope that Crookes was led, in 1861, to his first outstanding discovery. Over a long period of years Crookes gave much attention to the photography and study of the spectra of metals and other substances; and it may be recalled that when argon was discovered by Rayleigh and Ramsay in 1894 and helium by Ramsay in 1895, it was to Crookes, who was recognised as the most experienced observer of spectra and the highest authority in this direction, that the new gases were submitted for spectroscopic examination. It was by Crookes that the identity of terrestrial with solar helium was thereby definitely established.

Requiring, as he relates (*Chem. News*, 1861, **3**, 193), some tellurium for experimental purposes, Crookes recollected the residues which remained from the purification of crude selenium which he had kept untouched for ten years. Although the reactions of these residues seemed to show the presence of tellurium, Crookes tried in vain to isolate this element by chemical means. He resolved, therefore, to test for its presence by spectroscopic analysis. The result may be recorded in his own words: "A portion of residue introduced into a gas flame gave abundant evidence of selenium; but as the alternate light and dark bands due to this element became fainter, and I was expecting the appearance of the somewhat similar but closer bands of tellurium, suddenly a *bright-green line* flashed into view and quickly disappeared. An isolated green line in this portion of the spectrum was new to me. I had become intimately acquainted with the appearance of most of the artificial spectra during many years' investigation, and had never before met with a similar line to this; and as, from the chemical processes through which the residue had passed, the elements which could possibly be present were limited to a few, it became of interest to discover which of them occasioned this green line."

From the properties of the material Crookes was able to rule out the presence of all but five elements; and since the spectroscopic examination of these and of their compounds showed no trace of the green line, the conclusion was reached that this was due to a hitherto unknown element. To this new element Crookes gave the name *thallium*, "from the Greek θαλλός, or Latin *thallus*, a budding twig—a word which is frequently employed to express the beautiful green tint of young vegetation".

At first Crookes thought that this new element was related to sulphur, but the preparation and investigation of a number of its compounds soon convinced him that he was dealing with a metal;

and at the International Exhibition in 1862 he exhibited a specimen of thallium, in the form of a black powder, labelled as "a new metallic element discovered by means of spectrum analysis". Specimens of the oxide and sulphide were also shown. For his discovery of the new metallic element Crookes was awarded a medal by the authorities of the Exhibition.*

The discovery of thallium aroused much interest, partly because the use of the spectroscope was novel and partly because the properties of the new metal were strange. It exhibits the appearance and approximately the density of lead; some of its salts resemble those of lead and mercury, while others are similar in solubility and crystalline relations to the salts of the alkali metals. In those early days there were difficulties in deciding the particular family of elements in which thallium should be assigned a place. As is now well known, thallium can act as a univalent and as a tervalent metal.

Through his discovery of thallium Crookes at once secured a recognised position in the scientific world, and in 1863 he was elected a Fellow of the Royal Society, thus realising the first of his great ambitions.

The first obvious task which now lay before Crookes was the investigation of the chemical and physical properties of the new element and its compounds, and of its sources in nature (*Phil. Trans.*, 1863, **153**, 173). This task he carried out with great energy over a period of years. Among the most important of the physical constants was the atomic weight, and this he determined with masterly skill, thoroughness, and accuracy (see *Phil. Trans.*, 1873, **163**, 277). As Professor F. W. Clarke has recorded in his "Constants of Nature" (Smithsonian Institution, 1882): "In 1873, Crookes, the discoverer of thallium, published his final determination of its atomic weight. His method was to effect the synthesis of thallium nitrate from weighed quantities of absolutely pure thallium. No precaution necessary to ensure purity of materials was neglected; the balances were constructed specially for the research; the weights were accurately tested and all their errors ascertained; weighings were made partly in air and partly *in vacuo*, but all were reduced to *absolute* standards, and unusually large quantities of

* At the same Exhibition a solid ingot of thallium was shown by C. A. Lamy, Professor of Physics at Lille, who had independently discovered the element a year later than Crookes. While Crookes received the credit of discovering thallium, Lamy was awarded a medal for his production of a solid ingot of the new metal.

B

thallium were employed in each experiment. . . . Suffice it to say that *the research is a model which other chemists will do well to copy*. . . . Hence, using the atomic weights and probable errors previously found for N and O, Tl $= 203{\cdot}715 \pm 0{\cdot}0365$. If O $= 16$, Tl $= 204{\cdot}183$. . . . Crookes himself, using 61·889 as the molecular weight of the group NO_3, gets the value Tl $= 203{\cdot}642$; the lowest value in the series being 203·628 and the highest 203·666, an extreme variation of 0·038. This is extraordinary accuracy for so high an atomic weight, at least as far as Crookes's work is concerned." *

This passage illustrates the spirit which animated Crookes's work throughout. Nothing short of the highest attainable accuracy ever satisfied him.

In studying Crookes's progress in scientific research, one cannot but be impressed by the way in which he was led from one great discovery to another by taking up the investigation of any unusual or novel phenomena which might appear, a sign of the versatility and alertness of his mind. In the course of the determination of the atomic weight of thallium, irregularities in the weighings *in vacuo* were observed when the body weighed was either hotter or colder than the enclosure; and these effects were greatest at a certain degree of evacuation of the air.

Crookes was naturally intrigued by the strange effects he had observed and, thinking that he might obtain some relation between heat and gravity, such as Prof. Guthrie had considered probable (*Proc. Roy. Soc.*, 1868, **19**, 35), he investigated the effect of bringing a heavy metallic mass near to a delicately suspended light ball. He found that attraction or repulsion took place according as the heavy mass was hotter or colder than the ball. Experiment showed, however, that " whilst the action is in one direction in dense air, and in the opposite direction in a vacuum, there is an intermediate pressure at which differences of temperature appear to exert little or no interfering action " (*Proc. Roy. Soc.*, 1874, **22**, 37). The fuller investigation of the attraction and repulsion resulting from radiation occupied Crookes's attention for a number of years, during which he had the assistance of a young chemist, C. H. Gimingham, in carrying out a multitude of experiments and constructing the delicate apparatus required (*Phil. Trans.*, 1874, **164**, 501; 1875, **165**, 519). Many experiments were carried out with thin glass rods

* If one takes the now accepted value of 62·008 for the group NO_3, Crookes's value for the atomic weight of thallium is 204·03. The value now accepted is 204·39.

fitted at their ends with pith balls or discs and suspended by a silk thread inside a globe which could be exhausted. By irradiating one of the balls or discs, it was found that, at high exhaustions, repulsion took place, and this repulsion could be effected by irradiation not only with long heat waves, but also by radiations of all wave-lengths from infra-red to ultra-violet.

These experiments aroused much interest and discussion, and although he put forward no theory to account for the effects observed, Crookes suggested that his experiments might help, perhaps, to solve or throw light on some of the unsolved problems in celestial mechanics. Thus, he suggested, "in the sun's radiation passing through the quasi-vacuum of space we have the radial repulsive force, possessing successive propagation, required to account for the changes of form in the lighter matter of comets and nebulae ".

Continuing his experiments, Crookes examined the action of radiation on black and white pith balls suspended in a highly exhausted vessel, and was thereby led to the invention of the *radiometer*. This instrument, as described by its inventor, "consists of four arms, suspended on a steel point resting in a cup, so that it is capable of revolving horizontally. To the extremity of each arm is fastened a thin disc of pith, lamp-blacked on one side, the black surfaces facing the same way. The whole is enclosed in a glass globe, which is then exhausted to the highest attainable point and hermetically sealed." At the Anniversary Meeting of the Royal Society held in 1875, a Royal Medal was awarded to Crookes for his work. In presenting the medal, the President, referring to the radiometer, remarked : "It is the mystery attending this phenomenon that gives it its great importance. There is evidently some action going on with which we are not at present acquainted; and there is no saying what a thorough investigation into the cause of the phenomenon may lead to." Great interest was manifested by many experimenters in the phenomena observed, and there were many attempts at explanation. Ultimately, the explanation suggested by Dr. Johnstone Stoney was accepted. In the dark the gaseous molecules still present in the globe impinge equally on the two surfaces of the vanes and are thrown back with equal velocities. In the presence of light, however, the black surface absorbs the energy of radiation to a greater extent than the white, and thereby becomes hotter. The molecules are therefore repelled from it with a greater speed, and the recoil produces the observed rotation.

The invention of the radiometer caused a great sensation also in

non-scientific circles, and the instrument became a familiar object in almost every instrument-maker's window. Its vanes, spinning rapidly in the sunlight, could not fail to attract the attention of the passer-by or to excite his curiosity. Invitations to show and to lecture on the radiometer were received by Crookes from all parts of the country, and also from other countries, and helped to make his name more familiar to the general community.

From his experiments with the radiometer Crookes gained experience in the handling of highly attenuated gases; and from certain phenomena which he observed in the course of his experiments he was led to the investigation of the phenomena exhibited by the electric discharge through rarefied gas, which had already been studied by Plücker. On passing the discharge from an induction coil through a partially exhausted tube, the negative pole, or cathode, is observed to be surrounded by a dark space, known as the *Crookes*, or *cathode dark space*, separating the cathode from the luminous glow. This dark space enlarges as exhaustion proceeds, or as the pressure of the gas diminishes (*Proc. Roy. Soc.*, 1879, **28**, 110; *Phil. Trans.*, 1879, **170**, 135). Ultimately the dark space extends to the walls of the tube and the glass glows with a green phosphorescence. This phosphorescence Crookes attributed to the impact on the glass of a " fourth state of matter ", or " radiant matter ", which is as far removed from the condition of a gas as a gas is from a liquid. This " radiant matter", discharged from the cathode, was shown by Crookes to travel in straight lines, and he invented the well-known Crookes tube, in which a shadow is cast on the wall of the tube by a metal cross placed in the path of the radiation. Crookes also showed that the radiation, or stream of " radiant matter ", could be deflected by a magnet, and that when it is brought to a focus by the use of a cup-shaped cathode, the heat developed by its impact may suffice to melt platinum. In a lecture on " Radiant Matter", delivered before the British Association at Sheffield in 1879, Crookes concluded with the words: " In studying this Fourth state of Matter we seem at length to have within our grasp and obedient to our control the little indivisible particles which with good warrant are supposed to constitute the physical basis of the universe. We have seen that in some of its properties Radiant Matter is as material as this table, whilst in other properties it almost assumes the character of Radiant Energy. We have actually touched the border land where Matter and Force seem to merge into one another, the shadowy realm between Known and Unknown, which for me has always had

peculiar temptations. I venture to think that the greatest scientific problems of the future will find their solution in this Border Land, and even beyond; here, it seems to me, lie Ultimate Realities, subtle, far-reaching, wonderful."

In view of the brilliant researches carried out soon after by Sir J. J. Thomson one cannot but wonder at the scientific imagination and prophetic insight shown by Crookes in his postulation of the existence of radiant matter. Writing in 1902, he states (*Proc. Roy. Soc.*, 1902, **69**, 411): "In twenty-five years one's theories may change, although the facts on which they are based remain immovable. What I then called 'Radiant Matter' now passes as 'Electrons', a term coined by Dr. Johnstone Stoney to represent the separate units of electricity which is as atomic as matter. What was puzzling and unexplained on the 'Radiant Matter' theory is now precise and luminous on the 'Electron' theory." Advance of knowledge has thus justified the hypothesis of a "fourth state of matter", possessing high energy content and of a hitherto inconceivable fineness of subdivision.

In 1880, in recognition of his discoveries in molecular physics and radiant matter Crookes was awarded an extraordinary prize of 3000 francs and a gold medal by the French Académie des Sciences.

In 1880 Crookes moved into the house at 7 Kensington Park Gardens, stated to be the first house in England to be lighted by electricity, which remained his home for the rest of his life. There, in a well-equipped laboratory, he continued his scientific investigations, assisted often by subventions granted by the Royal Society.

It has already been noted that when an electric discharge takes place in a highly exhausted tube (Crookes Tube), the glass opposite the cathode emits a phosphorescent light under the impact of the "radiant matter" or cathode radiation; and Crookes also found that many other materials, including various minerals, especially diamond, similarly emit a more or less intense phosphorescent light of various colours. Crookes was naturally impressed by this phenomenon, and devoted some years to the spectroscopic examination of the phosphorescent light, and more especially to the characteristic discontinuous spectra given by the rare earths; substances which had aroused his interest while he was still a student at the Royal College of Chemistry, and which he spoke of as his first but not his only love. Crookes examined the phosphorescence spectra of many rare earth minerals, and was for long attracted and puzzled by the occurrence of a beautiful "citron" band, shown most

clearly by zircon. In tracking down the source of this band, he carried out a large number of separations of the rare earths and finally traced the band to yttrium. The band is given only faintly by yttria itself but most strongly by yttrium sulphate, the spectrum of which in a " radiant tube " was characterised by Crookes as " one of the most beautiful objects in the whole range of spectroscopy " (*Phil. Trans.*, 1883, **174**, 891). Later in his investigations of phosphorescence spectra, Crookes was greatly impressed by the spectrum of samaria, which shows an orange band. The spectrum was best given by the sulphate, more especially when mixed with calcium sulphate, and was," if anything, more beautiful than that of yttrium " (*Phil. Trans.*, 1885, **176**, 691).

The complicated relationships which are found to obtain in the phosphorescence spectra and the variability of the spectra brought about by admixture with other substances, although fully studied by Crookes in the course of his prolonged investigations, were not at first fully realised by him. When, therefore, he attempted to separate some of the rare earths, notably yttria, into the constituents of which they were supposed to consist, by means of a very elaborate scheme of chemical fractionation, he was, owing to his reliance on differences in the phosphorescent spectra, gravely misled into thinking that he had effected a separation of yttria into some eight or nine constituents. Later he realised that " one important lesson taught by the many anomalies unearthed in these researches is that inferences drawn from spectrum analysis *per se* are liable to grave doubt, unless at every step the spectroscopist goes hand in hand with the chemist ".

While Crookes, of course, could not fail to recognise the closely similar chemical characteristics shown by the rare-earth elements, the explanation of these chemical resemblances had to await the development of the electronic theory and the interpretation of the properties of elements in terms of the arrangement of the electrons within the atom. By his researches on the rare earths, however, Crookes was led to speculate on the nature of the elements and to the conception that the elements of the rare earths are made up of closely-related bodies or " meta-elements ". In his Presidential Address to the Chemical Society in 1888 Crookes said : " In defining an element let us not take an external boundary, but an internal type. Let us say, for example, the smallest ponderable quantity of yttrium is an assemblage of ultimate atoms almost infinitely more like each other than they are to the atoms of any other approxi-

mating element. It does not necessarily follow that the atoms shall all be absolutely alike among themselves. The atomic weight which we ascribe to yttrium, therefore, merely represents a mean value around which the actual weights of the individual atoms of the 'element' range within certain limits. But if my conjecture is tenable, could we separate atom from atom, we should find them varying within narrow limits on each side of the mean. . . . A similar absence of absolute homogeneity may possibly yet be traced in many of the 'elements' if once the right reagents are selected, and if laborious chemists are to be found willing to devote years to researches barren to outward seeming." Similarly, in his address to the Chemistry Section of the British Association in 1886 Crookes stated : "I conceive, therefore, that when we say the atomic weight of, for instance, calcium is 40, we really express the fact that, while the majority of calcium atoms have an actual atomic weight of 40, there are not a few which are represented by 39 or 41, a less number by 38 or 42, and so on". In Crookes's "meta-elements" we have the shadowy fore-runners of the isotopes, the existence of which was, at a later date, revealed by Soddy through the study of radioactive disintegration and confirmed by the experimental researches of J. J. Thomson and of Aston.

From the conception of the "meta-elements" Crookes was led to speculate on the genesis of the elements and definitely suggested an evolution of the elements from some few antecedent forms of matter, or possibly from only one *prima materia*.

"Going back to the 'fire-mist', the 'ur-stoff' of the German philosophers, or the 'protyle', as, after Roger Bacon, I have ventured to call it, we see an infinite number of immeasurably small ultimate, or rather ultimatissimate particles gradually accreting out of 'formless stuff', and moving with an inconceivable velocity in all directions. We find those particles which approximately have the same rate and modes of movement, beginning to heap themselves together by virtue of that ill-understood tendency through which like and like come together—that principle by virtue of which identical or approximately identical bodies are found collected in masses in the earth's crust instead of being uniformly distributed".

This suggestion had, indeed, been discussed from the early days of Greek philosophy, but the chemist had little positive information regarding the inter-relations among the recognised elements before the discovery of the periodic law. Taking an idea from Professor

Emerson Reynolds for the diagrammatic display of the periodic relation of properties to atomic weight, Crookes produced a figure-of-eight curve, on which the symbols of the elements are placed at intervals so that the members of natural families fall into position vertically over one another. On this curve the meta-elements would be ranged in groups or clusters close together.

For his researches on the behaviour of substances under the influence of the electric discharge in a high vacuum, with special reference to their spectroscopic behaviour, the Davy Medal was awarded to Crookes by the Royal Society in 1889.

The researches on the spark and phosphorescence spectra and other characters of the rare earths and of other substances engaged the attention of Crookes for more than twenty years. Towards the end of that period he carried out an extensive study of one of the rarest and least known of the recognised rare earths, scandia. A large number of minerals were examined for the presence of scandium, methods of extraction were worked out, a large number of salts, both organic and inorganic, were prepared and studied; and, as a result of Crookes's investigations, this element became one of the best known of the elements associated with the rare earth family (*Phil. Trans.*, 1908, *A*, **209**, 15; 1910, *A*, **210**, 359).

The spectra of elementary boron and silicon were the subjects of papers communicated to the Royal Society in 1912 and 1914.

The discovery of radioactivity by Henri Becquerel and of radium by Madame Curie towards the end of the nineteenth century naturally attracted Crookes's interest and attention. By the addition of ammonia to a solution of a uranium salt, in presence of traces of iron or aluminium, Crookes showed that the precipitate obtained showed strong radioactive properties, while the remaining uranium salt was almost inactive. To the active substance carried down by the precipitated iron or aluminium hydroxide Crookes gave the name Uranium-X. In the course of a year the uranium-X had lost and the uranium had regained its radioactivity, and from this uranium a further quantity of uranium-X could be precipitated. The action of radium rays (α-rays) on zinc blende having been pointed out to him, Crookes mounted a small piece of radium bromide in front of a screen of zinc blende at the end of a small tube fitted with a low-powered lens. With this little instrument, which Crookes called a *spinthariscope*, one could readily observe the tiny flash of light produced by the impact of an α-particle on the screen. Each flash is produced by the impact of one α-particle, and it is

therefore possible to count the number of α-particles emitted by a known weight of radium in a given time, as was done later by Lord Rutherford.

In 1908 Crookes drew attention to the remarkable resistance shown by the metals iridium and rhodium to the attack of all kinds of reagents, and discussed the advantages of these metals for use as crucibles in chemical laboratories (*Proc. Roy. Soc.*, 1908, *A*, **80**, 535). In 1912, also, while using an electric furnace, he was led to believe that platinum is not so entirely fixed, at temperatures well below the melting point, as had been thought; and he carried out a number of experiments on the loss of weight of the metals of the platinum group on being heated at 1300° and at 900°. At 1300° all the metals were found to lose weight, the percentage loss increasing in the order Rh $\rightarrow$ Pt $\rightarrow$ Pd $\rightarrow$ Ir $\rightarrow$ Ru. The loss of weight was much greater in the case of iridium and ruthenium than in the case of the others. At 900° platinum and rhodium showed no loss of weight on being heated for twenty hours. At 1300° platinum seems to volatilise *per se*, whereas the loss of weight of iridium is probably due to the formation of a volatile oxide (*Chem. News*, 1912, **105**, 229, 241).

Although his research work was carried out mainly in a spirit of a disinterested quest of knowledge and was, to use his own expression, without sub-stratum of utilitarianism, Crookes was also ready as occasion demanded, to place his knowledge and ability at the service of the community. In 1909, at the instance of the Glass Workers' Cataract Committee of the Royal Society, he undertook an investigation the main object of which was to prepare a glass which will cut off those rays from highly heated molten glass which injure the eyes of workpeople. This involved a study of the effects of the addition of a large number of metallic oxides to a colourless glass, specially prepared for the purpose by Mr. H. Powell, of the Whitefriars Glass Works. The problem was to prepare a glass which would cut off as much as possible of the heat radiation, while the colour would be scarcely noticeable when used in spectacles. Crookes extended the investigation so as to obtain glasses which would cut off ultra-violet rays and also diminish sun-glare. As a result, no fewer than eighteen different recipes were provided for glasses which satisfied the requirements in varying degrees (*Chem. News*, 1914, **109**, 265, 277, 289, 301).

It will be fitting to recall here some of the subjects which at various times during his long life were studied by Crookes who gave evidence

of possessing *not only an inexhaustible store of energy but also* varied interests.

In 1866 Crookes was appointed by the Government to report on disinfectants and their application to the arrest of the cattle plague which raged in England during 1865 to 1867, and it was he who was responsible for the recognition of the antiseptic value of carbolic acid.

Crookes interested himself, also, in the origin and formation of the diamond. While on a visit to Kimberley in 1896 he spent nearly a month in the mines studying the question of the origin of the mineral, and again in 1905, on the occasion of the visit of the British Association, he pursued the same enquiry. In 1893 Professor Moissan had claimed to have demonstrated the production of diamonds by crystallisation of carbon from molten iron under pressure, and *Crookes showed that the residue of cordite exploded* in a closed steel cylinder contains crystalline particles possessing the form of the diamond.* Crookes believed that diamonds had been formed in the earth by a process similar to that used by Moissan, or, alternatively, that all diamonds had originally been contained in meteorites. He published an interesting little book on diamonds in 1909.

In 1898 Crookes, in his Presidential Address to the British Association, discussed " The Wheat Problem ", and aroused the interest of the public by his warning that the supply of wheat, the staple foodstuff of Western peoples, might soon be insufficient to provide for the needs of the growing population unless the yield of the soil could be greatly increased by the application of much larger quantities of nitrogenous fertilisers; and that this, in turn, would in a *few years exhaust all the known sources of combined nitrogen.* As the discovery of any considerable new supplies of naturally occurring nitrogen compounds was scarcely to be relied on, there was an imperative demand laid on chemists to discover some means of forcing the inexhaustible store of elementary nitrogen in the air into such a state of combination that its assimilation by plants would be rendered possible. His views on the subject were embodied in a volume published a year later, in which he was able to reply to the various critics who in the meantime had questioned some of his conclusions. Though, doubtless, some of Crookes's most startling statements admit of modification, the topic was one of supreme

* The hard crystals which were thought by Crookes to be diamond, were later shown by Sir Charles Parsons to be incombustible in oxygen.

importance, and his warning probably did much to stimulate the development of the various processes which were later devised for the fixation of atmospheric nitrogen.

It would be almost impossible to enumerate all the various directions in which Crookes occupied himself in connection with problems of public interest, or as expert adviser to the Government; but mention may be made of his work on the disposal of town sewage; his reports on the composition and quality of daily samples of the water supplied to London, from 1880 to 1906; and his services as Consulting Expert on the Ordnance Board from 1907 onwards during the period of the First World War of 1914—18. With Crookes's numerous, frankly commercial activities we need not concern ourselves here.

Crookes's whole scientific career is interesting, apart from the value of his discoveries, as illustrating the fact that to a man of genius the character of his early education has, apparently, little influence on his later achievements. As already mentioned, Crookes left school at the age of sixteen, and at once specialised in a single branch of science under a teacher, eminent in his own field, but from whom the young student seems to have derived little but the advantage of example. The genius displayed by Crookes was accompanied by unusual independence of character, which was shown in a variety of ways, not only in the course taken by his own researches, but by his attitude toward the statements and pretensions of others. In pursuing his investigations, Crookes was guided largely by intuition, uninhibited by too wide a knowledge of the work of others, or by respect for theories. Nothing seemed too improbable to escape his attention, and, as Lord Kelvin is reported to have remarked, Crookes started more absolutely new hares than any other man among his scientific contemporaries.

The great services which Crookes rendered to science and to the community did not pass unrecognised or unrewarded, and numerous well-earned and fittingly conferred honours were showered upon him. His high reputation as a representative of science was recognised by the bestowal on him of the honour of knighthood in 1897, and honour was paid to his scientific discoveries by the award of the Royal, the Davy, and the Copley Medals by the Royal Society, of the Society's Medal by the Society of Chemical Industry, and of the Albert Medal by the Royal Society of Arts. Crookes's position of leadership in science was recognised by his election as President of the Chemical Society (1887—89),

as President of the Institution of Electrical Engineers (1890—94), as President of the British Association (1898), as President of the Society of Chemical Industry (1913), and finally as President of the Royal Society (1913—16). During his tenure of office he paid close attention to all the multifarious details of the business of each society. He served, also, as Honorary Secretary of the Royal Institution from 1900 to 1913, and as Foreign Secretary of the Royal Society from 1908 to 1912. The most distinguished Academies and Universities in the world acknowledged his eminence as scientist by election to their membership or the conferment of Honorary Degrees. In 1910 he received the crowning honour of his life when the King conferred on him the Order of Merit.

No account of William Crookes's life as a scientific man would be complete, and less than justice would be done to his personal character and independence of spirit, if all reference were omitted to the investigations in which, early in his career, he became involved concerning the phenomena of so-called "Spiritualism". The *Quarterly Journal of Science* for July, 1870, contains an article under the title "Experimental Investigation of a New Force", in which Crookes describes experiments undertaken with Mr. D. D. Home, a "medium" well known to the public at that time. At one of the earlier *séances* the experiments were made in the presence of Dr. Huggins (afterwards Sir William Huggins, President of the Royal Society), Serjeant Cox, proprietor and conductor of the *Law Times* and the *Recorder of Portsmouth*, one of Crookes's brothers, and his chemical assistant. Later, in January, 1874, the same journal published "Notes of an Enquiry into the Phenomena called Spiritual during the years 1870—73", with the signature William Crookes.

Anyone who has read these articles can realise the shock which was experienced by the scientific world on learning the character of the statements contained in them. Here was a well-known man of science, a Fellow of the Royal Society, the discoverer of thallium, with which and with its salts chemists had had time to become perfectly familiar, asserting in the most formal manner that in his presence things had been seen and done which everyone would regard as contrary to well-established natural law and to all ordinary experience.

It is perhaps not surprising that Crookes was publicly attacked in a violent manner, but he was able to show that many misrepresentations and misstatements were made which everyone must now perceive were wholly unjustifiable. The story of his experiences as

told by him is supported by evidence which would be accepted as conclusive if these statements related to any scientific work or to any ordinary occurrence. Crookes himself never withdrew or altered his statements concerning the phenomena he had witnessed, and in his Presidential Address to the British Association at Bristol, so late as 1898, he reiterated his conviction as to their reality. This conviction he retained to the end of his life. He was President of the Society for Psychical Research in 1897. His view, if he really had a settled opinion, as to the explanation of these strange phenomena cannot be given in his own words, but the view of Mr. Serjeant Cox on the theory of what he called psychic force is given very clearly at the end of the "Notes", and it appears probable, from the prominence given to this exposition, that it represents very nearly the opinion of Crookes himself. Perhaps the last few lines are sufficient to quote in this place, as probably views may have changed during the forty-five years since they were written. The passage is as follows: "The difference between the advocates of psychic force and the Spiritualists consists in this—that we contend that there is as yet insufficient proof of any other directing agent than the Intelligence of the Medium, and no proof whatever of the agency of the Spirits of the Dead; while the Spiritualists hold it as a faith, not demanding further proof, that the Spirits of the Dead are the sole agents in the production of all the phenomena. Thus, the controversy resolves itself into a pure question of *fact*, only to be determined by a laborious and long-continued series of experiments and an extensive collection of psychological facts."

On April 10th, 1856, Crookes married Ellen Humphrey, who "was considered very beautiful when she was young", the only child of William Humphrey, of Darlington in Yorkshire. With her he spent a long life of perfect companionship; their golden wedding being celebrated just a month before Lady Crookes died.

Crookes was a man of courteous and conciliatory manners, but his personality, it has been stated, was not specially impressive. "In his presence" wrote Sir Oliver Lodge, "one did not feel the worshipful enthusiasm which some of the great men of science have aroused". By his death, however, the world lost a great scientific pioneer who, throughout the whole span of his long life, was devoted to the advancement of science.

JAMES DEWAR

1842—1923

No greater service, it has been claimed, has been done to science in England than that rendered by Benjamin Thompson, a native of Massachusetts, who, as Count Rumford, a Count of the Holy Roman Empire, inspired the foundation in 1799 of the Royal Institution " for diffusing the knowledge and facilitating the general introduction of useful mechanical inventions and improvements; and for teaching, by courses of philosophical lectures and experiments, the applications of science to the common purposes of life ". Unique in character and purpose, the Royal Institution has attracted to its service men of the highest eminence in science; and the imposing building in Albemarle Street, London, with its many-columned façade, in which it is housed, has for nearly a century and a half been a centre of scientific discovery and invention, and of the popular exposition of science. No building in the world has been associated with so many classical and revolutionising investigations and discoveries; and no lecture-room is more famous than, or associated with the names of so many and so eminent lecturers as that still haunted by the spirit of Michael Faraday. To that Institution Dewar came, in 1877, as Fullerian Professor of Chemistry, and it became the chief centre of his experimental activities and, indeed, of his whole life. There he lived and laboured for forty-six years, enriching science by his investigations and fascinating the audiences who were attracted to his lectures, by the brilliance of his experimental demonstrations. The living-rooms on the top floor of the building, formerly occupied by Faraday and by Tyndall, in which he took up residence in 1887 as " Superintendent of the House ", became a centre of hospitality and a scientific *salon* where men and women, eminent in science, in art, in literature and drama, were wont to foregather. A lover of old furniture and *objets d'art*, Dewar furnished his rooms with choice tapestries and carpets, paintings, and engravings, and counted as one of his chief treasures a pair of bellows, " the chemist's first implement ", which he attributed to Benvenuto Cellini.

[Reproduced by permission of the Royal Institution.

JAMES DEWAR

James Dewar, the youngest of seven brothers, sons of Thomas Dewar, vintner, by his wife, Ann Eadie, daughter of a shipowner, was born on September 20th, 1842, at Kincardine-on-Forth, Scotland, a small town on the north bank of the Forth where the river widens out into the Firth. While still quite young he displayed a marked fondness for music, and before he was nine years of age could play the flute with some proficiency. In the winter of 1851—52 he met with an accident which broke the normal course of his young life and exercised an influence on the whole of his future career. One day, while he was skating, the ice broke and he fell into the ice-cold water. The chill which he received as a result of his immersion brought on an attack of rheumatic fever which crippled him for two years and, through impairment of the heart, cut him off permanently from all strenuous games and exercises. The period of comparative inactivity, however, was put to good account. Cut off from the normal companionship and games of boys of his own age, and receiving only a small amount of formal tuition, Dewar devoted himself with eagerness to reading; and the love of literature which was thereby developed remained with him throughout his life.

As the severity of his illness diminished, Dewar sought for means to satisfy his musical tastes, and, since he was now debarred by breathlessness from playing the flute, he turned to the violin. At that time the making of violins was a widespread art in Scotland, and Dewar, with the help of a local joiner, made several violins, to one of which, in the appropriate place, he attached a label, "JAMES DEWAR, 1854". This violin, still in existence, was played by a friend on the occasion of the golden wedding of Sir James and Lady Dewar in 1921. The period of enforced idleness due to his illness was held by Dewar to be the most instructive and stimulating epoch of his early life, and he attributed much of his later success as an experimentalist to the manipulative skill and dexterity which he acquired in making his violins. "The artistic use of my hands remains with me still," he said in 1921, "and I attribute my experimental aptitude entirely to my violin training."

When twelve years old Dewar was sent as a boarder to Dollar Academy, an independent, endowed school of high repute, lying at the foot of the Ochil Hills, where he distinguished himself especially in mathematics and natural philosophy. In 1859 he entered the Faculty of Arts of the University of Edinburgh, but the choice of a career had not yet been made. Attracted at first to the study of medicine, Dewar, at an early stage of his university life, came under

the influence of J. D. Forbes, Professor of Natural Philosophy, and of Lyon Playfair, Professor of Chemistry, whose Assistant he became; and his interests were thereby directed towards the physical sciences. While acting as Playfair's assistant, Dewar, in 1867, read a paper before the Royal Society of Edinburgh on the oxidation of "phenyl alcohol", and in connection therewith exhibited "a simple mechanical arrangement adapted to illustrate structure in the non-saturated hydrocarbons". By means of a number of thin bars of brass of equal length, Dewar constructed seven "meccano"-like models of the benzene molecule, including the well-known Kekulé formula and that which later became known as the Dewar formula. This work gained for Dewar an invitation from Kekulé to work in his laboratory, and the summer of 1867 was spent by Dewar in Ghent, where he not only gained inspiration from the great master of organic chemistry but derived much profit also from his association with the able experimentalist, Koerner. To this period belongs the conception by Dewar of the benzene-like structure of pyridine, the publication of which, however, was first made by Koerner (*J. Chem. Educ.*, 1934, **11**, 596). On Playfair's retirement from the Chair of Chemistry in 1868, Dewar became a demonstrator under Playfair's successor, Crum Brown, and had charge of the practical class for medical students.

Like van 't Hoff, Dewar obtained his first independent teaching post in a veterinary college, being appointed in 1869 Lecturer, and later Professor of Chemistry, at the Royal (Dick) Veterinary College, Edinburgh. He still continued to act as Assistant to Crum Brown till 1873, when he was appointed Assistant Chemist to the Highland and Agricultural Society of Scotland. During the two years he held this office Dewar delivered a number of lectures in different parts of the country.

The sixteen years which Dewar spent in Edinburgh constituted the period of character formation and of scientific upgrowth. A man of great innate ability, capable of mastering anything he willed to learn, and with a mind wide-ranging in its interests, Dewar not only passed from apprentice to master in science but entered also with zest and acceptance into the active and stimulating intellectual life of the Scottish capital. While gaining inspiration and delight from close contact with many eminent and remarkable men, he, in his turn, received a welcome from them on account of his scientific ability and social qualities. On August 8th, 1871, he married Helen Rose Banks, eldest daughter of William Banks, printer and engraver in Edinburgh.

Dewar's varied investigations, reported mainly in the *Proceedings* of the Royal Society of Edinburgh, and his active participation in the meetings of the British Association, gained for him widespread recognition and invitations to lecture in London. In 1873, he delivered a Friday evening lecture at the Royal Institution on the "Temperature of the Sun and the Work of Sunlight", and again, in 1875 and 1876, he delivered two lectures on "The Physiological Action of Light". In the second of these two lectures, in which he discussed the work which he had carried out in collaboration with Professor McKendrick, Dewar gave a model of the fascinating experimental demonstrations which became so conspicuous and looked-for a feature of his later lectures at the Royal Institution. In 1874 he gave a lecture before the Chemical Society on "Dissociation", a subject to which he had been attracted by the work of Sainte-Claire Deville. In this lecture he discussed the dissociation of carbon dioxide, of calcium carbonate, and of the compounds of ammonia with silver chloride and with calcium chloride, as well as the dissociation of salt hydrates and of "Graham's compound of palladium and hydrogen", as he called it. According to the report of the lecture in the *Chemical News*, "the lecturer concluded his able and interesting discourse with a description of an apparatus he had devised for ascertaining the temperature produced when a mixture of oxygen and hydrogen was exploded under various pressures". The method, which has since found repeated application, depended on measurements of the adiabatic compression of a given mass of air.

Happy as his years in Edinburgh no doubt were, and brilliant as the prospects of a distinguished career might have appeared to be, Dewar had not, at the age of nearly thirty-three, obtained a post satisfying to his ambition and worthy of his scientific achievements and promise. It must therefore have been with much satisfaction that, on April 13th, 1875, he learned that he had been elected, *more burgensium*, by the free vote of the resident Masters of Arts, Jacksonian Professor in the University of Cambridge.

Under the will of the founder, the professor was to be chosen for his knowledge of "Natural Experimental Philosophy and of Chymistry", but great latitude was allowed in the choice of the subjects on which he lectured. When the professorship became vacant in 1875 the majority of the electors favoured the view that the new professor should lecture on some aspect of chemistry, but a number desired that he should lecture on preventive medicine or on

physiology; * and it may be that Dewar owed his election, in part at least, to the fact that he had carried out researches on the constitution and physiological relations of cystine (in collaboration with the physiologist, Arthur Gamgee), and had also, more recently, collaborated with J. G. McKendrick in investigating the physiological action of light, of ozone, and of quinoline and pyridine bases.

One can well imagine the high hopes with which Dewar set out on his southward journey from the northern capital, to teach and work in a university where he could count Clerk Maxwell and G. G. Stokes among his colleagues. One cannot therefore but feel regret that these high hopes were not realised.

At that time Cambridge University offered only meagre facilities for research in the natural sciences, and the importance of promoting experimental science, in the advancement and development of which she later attained so great a fame, was but little recognised. Thus, the chemical laboratory of those days was a small, two-storied building, already overcrowded, and only one small room could be allotted to Dewar. A man highly individualistic in character, artistic in temperament, and impatient of restraints, devoted to activity in experimental research rather than to the greater passivity of the studious life, Dewar, coming from the freer, less cloistered intellectual and social life into which he had been admitted in Edinburgh, failed to adapt himself to the entirely different life and interests of the ancient English university. Had he possessed greater patience and tact, all might have been well; but, as has been recorded by one of his biographers, although no one could be more charming, he was often brusque in manner and over-emphatic in speech, and he estranged many of the senior members of the University in whom, in those mid-Victorian times, much of the old formality lingered. The Cambridge therefore of the 1870's, that delighted to recognise the genius of Clerk Maxwell and of Stokes, failed to appreciate the ability and originality of its young Jacksonian Professor.

At Cambridge, however, there began a lifelong friendship between Dewar and G. D. Liveing, at that time Professor of Chemistry, for whose personality and moral qualities Dewar had a great admiration; and for more than twenty years these two men collaborated in spectroscopic research, the results of which were published jointly

* The founder of the professorship in his will made the "serious request that the said Lecturer will in his Disquisition have an eye more particularly to that *opprobrium medicorum* called the gout".

and after Dewar's death were collected in a large volume, "Collected Papers on Spectroscopy". In 1882 Dewar was elected a Professorial Fellow of Peterhouse.

Although Dewar had, while in Edinburgh, delivered lectures at the Royal Institution and before the Chemical Society, residence at Cambridge enabled him to enter more fully into, and to play a more active part in the scientific life which found its centre in London; and in 1877 he was appointed Fullerian Professor of Chemistry at the Royal Institution, in succession to J. H. Gladstone. Dewar's chief interests were now transferred from Cambridge to London and, full of reverence for his great predecessor, Faraday, by whose spirit he constantly felt himself encompassed, and proud of the traditions of the Royal Institution, he devoted himself wholeheartedly to its service. Although he retained the Jacksonian professorship at Cambridge until his death, the Royal Institution became the sole object of his affection and the centre of his life and work. When, through the munificence of Dr. Ludwig Mond, the Davy-Faraday Laboratory was founded in 1896, Dewar became its first Director.

Dewar had little or nothing of the pedagogue in him; the instructing and training of undergraduates had no interest for him. Even his research work was highly individualistic, and demanded not only an active mind but great manipulative skill. He preferred to carry it out himself, assisted by young scientists and able technicians. He built up, therefore, no school of research, and he gathered around him no large body of young chemists whom he could inspire with his own intense love of research or to whom he could pass on his own characteristic scientific outlook and methods of work.

At the Royal Institution, Dewar experienced a feeling of emancipation. There he found himself in free control of a laboratory which, certainly, was far from being lavishly endowed, but which offered much greater experimental facilities than Cambridge could at that time supply, and he was able to plan his life and work as he pleased, free from the regulations and restraints, the fixed routine of lecturing and instructing, to which a university teacher is necessarily subject. Lectures, it is true, had to be delivered at the Royal Institution, "courses of philosophical lectures and experiments" had to be provided, but the lecturer was free to choose the subjects on which he desired to discourse. The type of these lectures appealed to Dewar's artistic temperament. As a lecturer, Dewar could not achieve the lucid and captivating style for which his predecessor, Tyndall, was noted, but, gifted with exceptional powers of imagination and with

an extraordinary command of technique, he brought the art of lecture illustration by experiment to a marvellous degree of perfection. During his tenure of office at the Royal Institution, Dewar delivered many of the afternoon lectures, Friday evening discourses, and lectures to juvenile audiences for which the Institution has gained so great a fame, and he held his audiences, old or young, spellbound by his ingenious and striking demonstrations, to the preparation and rehearsal of which he devoted much time and thought.

Although Dewar's interests lay mainly in the prosecution of research solely for the advancement of knowledge, his eminence as a chemist led to his being widely consulted by the Government, by Municipalities, by industrial corporations, and by others. In 1888 he was appointed a member of the Explosives Commission set up by the Government, and was the inventor, in association with Sir Frederick Abel, of the smokeless propellant, cordite. For many years he served with Sir William Crookes on the Metropolitan Water Board, making daily reports on the purity of the London water supply, and he was frequently consulted on problems of water purification and sewage disposal.

Dewar's scientific life was one of extraordinary productivity. Although his earliest investigations were in the domain of organic chemistry and biochemistry, his interests in physical and physico-chemical research soon became apparent, and his first extended series of investigations, initiated at Cambridge, was in the field of spectroscopy. The work with which his name will always be most closely associated is that dealing with the liquefaction of gases, the properties of substances at low temperatures, and the production of high vacua. Dewar's interests, however, were wide and few chemists can have excelled him in the volume and variety of the investigations which he carried out, either alone or in collaboration with others. An impressive record of his scientific work is contained in the volume "Collected Papers on Spectroscopy", already referred to, and in the two large volumes of "Collected Papers of Sir James Dewar".

His eminence as a scientist and the importance of his many contributions to knowledge were universally recognised, and he was given many honours. Honorary degrees were conferred upon him by no fewer than eleven universities, British and foreign, and the leading Academies of Science in the United States of America and in Europe enrolled him as one of their members. His eminence as a chemist was recognised by his election as President of the Chemical

Society (1897—99), and as President of the Society of Chemical Industry (1887); and his election as President of the British Association in 1902 gave testimony of his outstanding distinction as a representative of British science.

In his Presidential Addresses, Dewar gave evidence of his special interest in the more philosophical and cultural aspects of chemistry and in the extension of education in science in this country. Perturbed, as many other chemists of his time were, by the neglect of science, Dewar warned the leaders of industry that "industrial supremacy is not an inalienable possession which one generation can hand down to another with perfect security, but that it is, on the contrary, an unstable possession which can only be maintained and held through scientific intelligence and cultivated industry". His own aims, ambition, and outlook in science were well reflected in the words with which he concluded his presidential address to the British Association: "To serve in the scientific army, to have shown some initiative, and to be rewarded by the consciousness that in the eyes of his comrades he bears the accredited accolade of successful endeavour, is enough to satisfy the legitimate ambition of every earnest student of Nature. The real warranty that the march of progress in the future will be as glorious as in the past lies in the perpetual reinforcement of the scientific ranks by recruits animated by such a spirit, and proud to obtain such a reward."

Fitting honour, also, was paid to the importance and distinction of Dewar's scientific achievements by the award of the Rumford, Davy, and Copley Medals by the Royal Society; of the Albert Medal by the Royal Society of Arts; of the Society's Medal by the Society of Chemical Industry; of the Hodgkins Medal by the Smithsonian Institute, Washington; of the Franklin Medal by the Franklin Institute, Philadelphia; of the Lavoisier Medal by the French Academy of Science; of the Matteucci Medal by the Italian Society of Science; and of the Gunning Victoria Jubilee Prize by the Royal Society of Edinburgh. For his service to science and the community he received the honour of knighthood in 1904.

Slight of build and of medium height, Dewar had an acute and versatile mind, and a poise of manner that was evidence of sureness of self and of independence of character. A man of wide interests and cultivated mind, he enjoyed the friendship of leaders in the fields of science, art, literature, and the drama; and he possessed a charm of manner which won for him the steadfast friendship and affection of many. Of an inherently generous nature, Dewar, when

the need arose, gave his help unstintingly to anyone with whom he was associated, and the earnest student or worker could be sure of his sympathy and encouragement. He had, however, the defects of his qualities, the ever-present flaws of nature's gems, and his impatience of opposition, accentuated perhaps by his suffering from sleeplessness, led sometimes to a brusqueness of manner and roughness of tongue which hurt and estranged. He was a great man, full of vigour and with a kind, if combative, disposition.

The esteem and affection in which Dewar was held by his friends and fellow-chemists were shown by the presentation to him, by members of the Royal Institution, of a golden loving cup in celebration of his golden wedding, and by his entertainment as guest of honour at the Anniversary Dinner of the Chemical Society in 1921. Of this honour, paid to him by those who knew him best towards the end of a long life dedicated to the service of science and full of distinguished achievement, Dewar showed his appreciation, and disclosed also his innate humility in the words: "Although I have done my share of work, do not overload me with honour.

'Be those men praised of us,
Who have loved and wrought and sorrowed and not sinned,
For fear or fame or gold,
Nor waxed with winter cold,
Nor changed with changes of the worldly wind.'

If the new Fellows of the Chemical Society I have been privileged to see arise think I have the shadow of a claim to be included in the poet's definition, then I wish no further reward for merit."

The coming of the war of 1914—18 made it impossible for Dewar to continue his work with liquefied gases, and he found solace to his soul by turning again to the study of soap films and soap bubbles, which had formed the subject of his first course of Christmas Lectures to young people in 1878. As a pure experimentalist, he elucidated the conditions necessary for the production of long-lived bubbles and flat films of great size, and studied the interference colours displayed when a jet of air was made to play upon their surface. Soap bubbles, 42 cm. in diameter, were shown at the Royal Society on June 22nd, 1916.

Knowing that the setting of the sun was near, Dewar continued actively engaged in scientific investigation to within a few days of his death, on March 27th, 1923, thus realising his own desire, expressed in the words of Walter Pope, found open on his working table:

"To outlive my senses may it not be my fate,
To be blind, to be deaf, to know nothing at all,
But rather let Death come before 'tis too late,
And while there's some sap in it may my tree fall."

The research work carried out by Dewar during his Edinburgh period was of a varied character and gave evidence of his wide and lively interest in various branches of science rather than of special devotion to one of them. It was a period of apprenticeship, of "learning to exercise his genius"; and his investigations were prompted by circumstance and opportunity rather than by creative imagination. Essentially an experimentalist, Dewar carried out his investigations in many different directions—specific heat of carbon at high temperatures, specific heat and physical constants of "hydrogenium", researches in very perfect vacua, etc.—but they were, to a considerable extent, tentative in character and were not, at the time, pushed to completion. Some of the problems, however, which he then attacked somewhat superficially were subjected to a more thorough investigation in later years.

On migrating to Cambridge, Dewar took up again the investigation of coal-tar bases, and especially of compounds of the quinoline series, studying, in particular, the oxidation of leucoline from coal tar, which was shown to be a mixture of at least two isomeric bases. Other interests developed, however, and investigations in the domain of organic chemistry were not again pursued. Dewar now began to cultivate with thoroughness a definite area of science, and undertook, in collaboration with Professor G. D. Liveing, an extended series of spectroscopic investigations. In adopting this field for research, Dewar was prompted, so it has been suggested, by his great interest in the work of Sainte-Claire Deville on dissociation and by Lockyer's speculations on the dissociation of the elements at high temperatures.

Dewar's appreciation of the significance of the spectroscope in physics and chemistry is evident not only from the diversity of problems to which he applied it, but also from his own comment upon it as "the most powerful method of analytical investigation yet devised". That he also realised the delicacy and sensitivity of the new technique is clear from the extreme care taken in correlating new spectral lines or bands with the atoms or molecules giving rise to them. Indeed, he concludes that the spectrum of a gas in a rarefied state affords the most delicate test of its purity. This was at a time some twenty years before the advent of the quantum

theory, and thirty or forty before atomic and molecular spectra were interpreted satisfactorily in terms of molecular dynamics. Even now, with guidance from such theoretical principles, the unambiguous correlation of observed spectra with a particular emitter often proves difficult; in the absence of such guidance Dewar's careful design of experiment and cautious deductive argument were exemplary. All this work reveals a true love of experiment, and the desire to discover, describe, and explain natural phenomena. By modern standards the equipment available was primitive and the general facilities meagre, but this only makes the achievement the more remarkable.

Dewar's first interest was the interpretation of solar absorption lines, and a study was made of the reversal of spectral lines of metallic vapours. This was later extended to a study of the ultra-violet emission lines of many metals, and to the general consideration of the conditions affecting the excitation of spectral lines. The differences between the arc, spark, and flame spectra of magnesium and other metals were also examined. The contrast between single spectral lines, or multiplets, on the one hand and groups of lines (bands) on the other, occupied Dewar's attention, and, although he did not fully appreciate the true significance of the differences, he showed meticulous care in attempting to identify the emitting agents. He photographed the " water " bands in the middle ultra-violet, now identified with the hydroxyl radical, and studied the band systems of magnesium oxide and hydride, of nitrogen, and of carbon monoxide. His controversy with Lockyer about the origin of the so-called "nitrocarbon bands" provides a typical example of his caution, for after assembling and discussing all experimental results he concluded that the bands were attributable to a compound of nitrogen and carbon—then regarded as cyanogen.

Dewar also studied the absorption spectra of some simple molecules including the halogens, sulphur dioxide, hydrogen sulphide, carbon disulphide, and chlorine peroxide, and examined the continuous emission of a spark under water. He investigated the spectral absorption of liquid oxygen, the emission from flames of burning nickel carbonyl and metal alkyls, and from gaseous explosions, and the emission spectra of the inert gases. Another problem studied was that of the absorption lines of rare-earth salts in solution, and the effect on them of temperature, concentration, and solvent. This wide variety of subjects, each of interest today, suffices to show the scope of his work, and the manner in

which he sought to apply the results to all relevant phenomena gave further evidence of his vision.

Neither at Cambridge nor at the Royal Institution did Dewar restrict his research work to spectroscopic investigations. His interests led along many different paths. In 1873, in Edinburgh, Dewar, in collaboration with William Dittmar, had begun the determination of the vapour density of potassium; and this work was taken up again at Cambridge in collaboration with Alexander Scott. The method of Victor Meyer was employed, using a vaporisation tube of platinum, and values of the vapour density were obtained which indicated the monatomic nature of the molecule of potassium and of sodium. Determinations of the atomic weight of manganese, by analysis of silver permanganate, and of the molecular weight of triethylamine were also carried out; and in these days it is perhaps of interest to recall that the object of these investigations was the testing of Prout's law, the near approach of a number of atomic weights to whole numbers being, at that time, " still a matter of very serious suggestive interest ".

Soon after his appointment as Fullerian Professor at the Royal Institution, also, Dewar took up the study of chemical reactions at the temperature of the electric arc and showed that when carbon, nitrogen, oxygen, and hydrogen are present at this high temperature, hydrocyanic acid, acetylene, and nitrous acid are invariably formed.

In 1877, however, a new direction began to be given to Dewar's thoughts and interests by the work of Pictet and of Cailletet on the liquefaction of gases. This work not only created a stir among men of science but aroused also the interest of the layman; and in the summer of 1878 Dewar, in one of his Friday evening discourses at the Royal Institution, showed Cailletet's apparatus in action. Impressed by the achievements of Pictet and of Cailletet and later, in 1884, by those of the Polish scientists, Wroblevski and Olszevski, which made possible the production, in moderate quantity, of liquid air, oxygen, and nitrogen, Dewar, somewhat tentatively at first and then with evergrowing intensity and devotion, took up the task of exploring the approaches to the absolute zero of temperature. This, indeed, was a task which might be regarded as one most properly to be undertaken by the successor of Davy and of Faraday, pioneers in the liquefaction of gases, and one which could not fail to arouse Dewar's enthusiasm and make appeal to his artistic longing for novelty of effect. Dewar's purpose in undertaking this work was not so much to achieve the liquefaction of refractory gases, although

in this direction, also, he was notably successful, as to investigate the properties of matter under unusual and hitherto unattainable conditions. "He was never", as H. E. Armstrong has recorded, "the mere artificer, but always the philosopher seeking to penetrate into the far distant region of the ultimate zero of temperature". It was a scientific exploration into an unknown region which he undertook, a pioneering exploration which required genius and experimental resourcefulness, untiring energy, and courage to face great possible risks. Dewar was fortunate in the possession of these qualities, and his achievements entitle him to a position of the highest eminence among those who have engaged in low-temperature research. Although, in the course of his work on the liquefaction of gases, two of his assistants each lost an eye, Dewar, as Lord Rayleigh has recorded, never admitted that anything was dangerous. The most he would say was that it was a little tricky.

In his march towards the absolute zero, Dewar first produced liquid oxygen and liquid air, in quantities never before attained, by compressing these gases at the temperature of liquid ethylene, boiling under reduced pressure, or by using liquid ethylene and solid carbon dioxide, cascade fashion, as refrigerants. After 1895, however, he made use of the Joule–Thomson effect, or the cooling produced by the expansion of a compressed gas through a nozzle. Although by this method pre-cooling of the air was not necessary, Dewar always used solid carbon dioxide as a pre-cooling refrigerant; and a large machine was built which was capable of producing twenty litres of liquid air per hour. This was done in preparation for the next advance, the liquefaction of hydrogen.

The production of liquid hydrogen in a form which could be collected was accomplished by Dewar as the outcome of a long series of efforts, frequently baffled but persistently renewed. The difficulty of the problem can be realised when it is borne in mind that the critical temperature of hydrogen is $-241°$, whilst the lowest temperature attainable by means of liquid air, boiling under reduced pressure, is in the neighbourhood of $-200°$. Dewar sought to bridge the gap by mixing hydrogen with from 2 to 5 per cent. of nitrogen or of air, so as to obtain a gas which might be liquefied by means of liquid air. The results, however, obtained down to 1894 were summed up by Dewar in the words: "One thing can be proved by the use of the gaseous mixture of hydrogen and nitrogen, *viz.*, that by subjecting it to a high compression at a temperature of $-200°$, and expanding the resulting liquid into air, a much lower

temperature than anything that has been recorded up to the present time can be reached. This is proved by the fact that such a mixed gas gives, under the conditions, a paste or jelly of solid nitrogen, evidently giving off hydrogen because the gas coming off burns fiercely. Even when hydrogen containing only some 2 to 5 per cent. of air is similarly treated the result is a white, solid matter (solid air) along with a clear liquid of low density, which is so exceedingly volatile that no known device for collecting it has been successful."

A notable advance was made when, in 1895, Dewar showed that if hydrogen, cooled by a bath of liquid air at $-200°$, is forced at 200 atm. through a fine nozzle over a regenerative coil previously cooled to the same temperature, a jet of gas along with a liquid could be seen. Although no liquid could then be collected, it appeared certain that, by suitable construction of the apparatus, liquid hydrogen would be obtained. In order to demonstrate the low temperature which is produced in the jet of hydrogen, Dewar sprayed liquid air and oxygen with the hydrogen jet, and found that in a few minutes the liquids were transformed into hard white solids, "resembling avalanche snow", quite different in appearance from the jelly-like mass of solid air got by the rapid evaporation of the liquid under reduced pressure. Thus, for the first time, solid oxygen was obtained. Although Dewar had so far failed to obtain solid oxygen by rapid evaporation of the liquid, he later, in 1911, succeeded in doing so. The reason why oxygen differed from nitrogen and, as shown later, from hydrogen, was that the vapour pressure of solid oxygen at its melting point is much lower than that of solid hydrogen or solid nitrogen. By causing liquid oxygen, well insulated thermally, to boil under a pressure maintained below 0·1 mm. by means of charcoal, solid oxygen could be obtained.

Solid oxygen has a pale-bluish colour and shows by reflection all the absorption bands of the liquid. It was found to melt at 46° K. under a pressure of 0·9 mm.

The success attained by Dewar in producing the hydrogen jet led him to construct a much larger liquid air plant (to which reference has been made), and to combine with it circuits and arrangements for the liquefaction of hydrogen. The apparatus, the detailed construction of which Dewar, being somewhat secretive in such matters, never made known, took a year to build; and many months were occupied in testing and preliminary trials. Defeats and failures were encountered, but at last success was achieved. Here is the account

given by Dewar: "On May 10, 1898, starting with hydrogen cooled to −205° C. and under a pressure of 180 atmospheres, escaping continuously from the nozzle of a coil of pipe at the rate of about 10 to 15 cu. ft. per minute, in a vacuum vessel doubly silvered and of special construction, all surrounded with a space kept below −200°, liquid hydrogen commenced to drop from this vacuum vessel into another doubly isolated by being surrounded with a third vacuum vessel. In about five minutes, 20 c.c. of liquid hydrogen were collected when the hydrogen jet froze up, from the accumulation of air in the pipes frozen out from the impure hydrogen. The yield of liquid was about 1 per cent. of the gas. The hydrogen in the liquid condition is clear and colourless, showing no absorption spectrum, and the meniscus is as well defined as in the case of liquid air." The first demonstration of liquid hydrogen was given by Dewar at a lecture in commemoration of the centenary of the Royal Institution in 1899. On the lecture table stood a litre of liquid hydrogen in a vacuum vessel standing in liquid air.

By means of liquid hydrogen, a temperature lower than any hitherto known was attained. It was the coldest liquid then known. Under ordinary atmospheric pressure it was found to boil at −252·5° Reduction of the pressure by an air-pump brought the temperature down to −258°, when the liquid passed into a solid resembling frozen foam, and this, by further exhaustion, was cooled to −260°. Solid hydrogen could also be obtained in the form of a clear, transparent ice, melting at about 15° K. under a pressure of 55 mm. It had a density one-eleventh that of water. By its means every gaseous substance, except one, could be obtained in the solid form. When the vapour of boiling liquid hydrogen was allowed to escape into the air a dense surging snowstorm of solid air was produced.

The lowest temperature attainable by means of hydrogen was still 13° above the absolute zero. To what extent could this gap be bridged?

Further progress towards the absolute zero depended on finding a substance which, in the liquid state, was more volatile than liquid hydrogen; and helium, discovered by Ramsay in 1895, was such a substance. In his Presidential Address to the British Association in 1902, Dewar discussed the possibility of liquofying helium, the boiling point of which, there was reason to believe, would probably be about 5° K. Provided the critical point was not below 8° K., Dewar considered it safe to predict that it would be possible to liquefy helium by a method similar to that employed for the lique-

faction of hydrogen, the helium, however, being pre-cooled by liquid hydrogen, instead of liquid air, boiling under reduced pressure. It was on these lines that Dewar proposed to attempt the liquefaction of helium.

Dewar realised that the practical difficulties and the cost of the operation would be very great, for at that time the presence of helium in natural gas was not known and the production of helium from monazite was a laborious and costly process. The late Lord Rayleigh, however, had found that the gas bubbling up from the hot spring at Bath contained some argon and helium, and Dewar decided —very unfortunately, as it happened—to use the Bath spring as the source of helium. The gas was collected, compressed into cylinders, and transported to London, where it was treated for the extraction of helium, which formed only one-thousandth part of the whole. This helium Dewar sought to liquefy by expansion, with regenerative cooling, of the compressed gas pre-cooled with liquid hydrogen boiling under reduced pressure. The present Lord Rayleigh, who saw Dewar's apparatus in course of construction, has given the following description of it: "The regenerative coil was contained in a vacuum glass. Outside this was a larger vacuum glass to contain liquid hydrogen and outside this again a simple glass cylinder to contain liquid air. The outer glass vessels were to afford thermal insulation. The liquid helium, had it appeared, could only have been examined through no less than seven separate glass walls, or fourteen surfaces." Unfortunately, liquid helium did not appear; and the principal obstacle which prevented the success of Dewar's attempts to liquefy the gas appears to have been the blocking of the tubes and valves with solid neon, which was present, unsuspected, in the gas from the Bath spring and could not readily be removed by the methods of purification adopted. The blocking of the tubes had been attributed, at the time, to other impurities which had escaped removal. Dewar must, no doubt, have suffered acute disappointment when, in 1908, Kamerlingh Onnes, employing the same method as he had done, but using helium extracted from monazite, succeeded where he had failed. It is proper to record, however, that Dewar took his disappointment with good grace and himself gave an exposition of Kamerlingh Onnes's work at a meeting of the British Association in Dublin in 1908.

By means of liquid helium boiling under reduced pressure one was able to approach to within less than 1° of the absolute zero.

When, after 1895, the production in quantity of liquid oxygen and

liquid air made possible the prosecution of research at low temperatures, the necessity of devising some new kind of vessel for storing and manipulating such volatile liquids soon became apparent. All attempts at improvement on the principle of using a succession of surrounding glass vessels, the space between which was cooled by the current of vapour from the boiling liquid, met with failure. The difficulties which were encountered, however, were overcome by Dewar through his invention of the vacuum-jacketed flask. Few inventions have been of greater importance for the advance of knowledge. As Kamerlingh Onnes, speaking in 1904 of Dewar's invention of the vacuum-jacketed vessel, said : " an entirely new path was struck by Dewar with respect to investigations at low temperatures. . . . Dewar's magnificent invention may be called the most important appliance for operating at extremely low temperatures. The open vacuum flasks are for the permanent gases what the steel bottles, tested at 250 atmospheres, are for the coercible gases. In fact, the moment when a vacuum glass containing liquid oxygen was offered to the Prince of Wales at the meeting of the Royal Institution marks a new era in low temperature research."

The vacuum-jacketed flask, under the name " thermos flask ", later became available to the general public as a convenient and efficient storage vessel for hot or for cold liquids.

The insulating properties of a vacuum in preventing the influx of heat to a vessel by the elimination of convection currents had long been known to the physicists; and this insulating action was first made use of by Dewar in 1873 in calorimetric determinations of the specific heat of hydrogen occluded in palladium. When, therefore, Dewar came to study the properties of liquefied gases of low boiling point, the idea of using a vacuum-jacketed vessel in which to contain the liquids naturally suggested itself; and an account of the experiments which led up to the use of such vessels was given in a Friday evening discourse at the Royal Institution on January 20th, 1893. Various forms of vessel were constructed in glass, and many experiments were carried out for the purpose of increasing their efficiency. Originally, the air between the inner and outer vessels was exhausted by means of a Sprengel pump, and it was found that the thermal insulation was improved by filling the exhausted space with various finely divided solids, such as silica, lampblack, and bismuth oxide. Still more effective insulation, however, was obtained by silvering the inner surfaces of the glass vessels, the radiation influx being thereby very greatly diminished. By these

means the rate of evaporation of liquid air could be reduced to one-thirtieth of its value when the vessel was surrounded by air.

Since the heat-insulating quality of the vacuum-jacketed vessel is largely dependent on the state of exhaustion of the space between the inner and outer vessels, a considerable advance was made through the application of the discovery, made by Dewar in 1905, of the great increase in the adsorptive power of charcoal at low temperatures. Even as early as 1874, while working in collaboration with Professor P. G. Tait in Edinburgh, Dewar made use, for the first time, of the adsorptive power of charcoal for the purpose of obtaining high vacua, the adsorption taking place at the ordinary temperature. In 1905, however, while studying the heat evolved in the adsorption of different gases by charcoal at −185°, Dewar found that a very considerable increase of adsorption takes place at this low temperature as compared with the adsorption at the ordinary temperature. The numbers obtained by Dewar are given in the following table :

	Volume (c.c.) adsorbed per gram of charcoal at 0°	at −185°
Helium	2	15
Hydrogen	4	135
Electrolytic gas	12	150
Argon	12	175
Nitrogen	15	155
Oxygen	18	230
Carbonic oxide	21	190

By placing a small quantity of charcoal in a globular recess in the vacuous space of the flask and filling the vessel with liquid air, the charcoal was cooled and adsorbed the remaining traces of air. A very high vacuum was produced, and the heat-insulating qualities of the vessel were thereby greatly increased.

The employment of charcoal at low temperatures for the production and maintenance of a high vacuum made it possible to use metals, such as copper or nickel, instead of glass for the construction of vacuum-jacketed vessels. Metals give off, for a long time, small quantities of gas which would impair the vacuum and so diminish the heat-insulating qualities of the vessel. Through the presence, however, in the vacuous space of charcoal which is cooled to a low temperature by the liquid air or other liquid of low boiling point placed in the vessel, the vacuum can be maintained and the heat-insulating qualities preserved.

The production of high vacua by means of charcoal cooled to a low temperature contributed to the success of the earlier researches

on positive rays and on the rate of generation of helium from radioactive substances, and proved also of the highest value in many other fields of research. The different condensability of gases on charcoal at low temperatures gives one of the most rapid means of separating or concentrating the constituents of a gas mixture. If, for example, air is passed over charcoal cooled to $-185°$, oxygen is preferentially adsorbed, and, when the temperature of the charcoal is allowed to rise, the adsorbed gas which is evolved is found to contain 56 per cent. of oxygen. If the adsorbed gas is collected in fractions as the temperature rises, the fractions become increasingly rich in oxygen, and the end fractions may contain upwards of 84 per cent. of that gas. By means of charcoal at low temperatures, also, the rare gases can be separated from air.

Owing to the relatively small amounts of liquefied gases then available, Dewar's earliest investigations at low temperatures, begun in 1883—84, were, for the most part, restricted to simple determinations of the properties of the liquids, such as molecular volume, boiling point, critical temperature, and critical pressure. Such determinations were made on ammonia, hydrogen sulphide, cyanogen, methane, and ethane. When, however, in the early 'nineties, liquid oxygen and liquid air, and later liquid hydrogen, became available in quantity, and after the storage and handling of these liquids had been made easy by the introduction of vacuum-jacketed vessels, a wide range of properties of substances at low temperatures could be studied. For many years the whole field of low-temperature research was actively explored. At the low temperatures then readily attainable the intensity of chemical reaction was found to be greatly diminished, and the colours of many substances changed. Uranium nitrate and the double chloride of platinum and ammonium become white; the oxide, sulphide, and iodide of mercury become yellow; and the colours of chromic acid, solutions of iodine in alcohol, etc., are greatly changed. Young's modulus of elasticity is increased to 4—5 times its value at the ordinary temperature when a metal wire is cooled in liquid air, and the tenacity, or breaking stress, is increased by 20—50 per cent. of its ordinary value.

In 1892, Dewar, in collaboration with J. A. Fleming, Professor of Electrical Engineering at University College, London, began an extensive investigation of the electrical and magnetic properties of pure metals and of metal alloys, and, later, determined the dielectric constants of a number of substances.

The general object of their first investigations was the deter-

mination of the specific electrical resistance of metals and alloys between the limits of temperature of about 200° and the lowest attainable temperatures approaching the absolute zero; and they particularly desired to investigate the variation of resistance with temperature below −100°, and to determine the form of the temperature–resistance curves as the temperature is lowered down to the lowest point attainable by the evaporation of liquid oxygen boiling under reduced or normal pressure.

When the variation of resistivity with temperature is represented graphically, with temperatures as abscissae, the curves for the pure metals all converge downwards in such a manner as to indicate that the electrical resistance would vanish at the absolute zero of temperature. This was the first indication of a behaviour later confirmed by the investigations of Kamerlingh Onnes at the temperature of liquid helium. No such convergence is found in the curves for alloys. The slightest impurity in a metal changes the position of the resistance curve. With some metals, the curves of resistivity intersect, so that the order of resistivities at low temperatures may be different from that at ordinary temperatures. Thus at 13° pure silver is the best conductor, but at −200° pure copper is a better conductor than silver.

The resistivity curves of some metals are very much bent. The principal magnetic metals—iron and nickel—have curves which are very convex towards the temperature axis, and this behaviour is shown also by many magnetic alloys. The percentage decrease in resistance on cooling from +200° to −200° is greater than with any other metal. These magnetic metals, it is noted, have smaller atomic volumes than any other metal, and it is found that, in general, the worst conductors among the metals are those with large atomic volumes and large valency.

When one pure metal is added in small amount to another pure metal, the resistivity curve is raised almost parallel to that of the predominant constituent; and when two pure metals are alloyed together in various proportions, there is generally some proportion in which the resultant alloy has a maximum resistivity and, except in the case of alloys of zinc, tin, lead, and cadmium with each other, the resistivity of the alloy is greater than that of either of its constituent metals.

Nickel–steel alloys with a large percentage of nickel can exist over wide limits of temperature in two different states, in one of which the alloys are strongly magnetic, and in the other only feebly

magnetic. On cooling to low temperatures they pass from the non-magnetic into the magnetic condition. Since the resistivity of the non-magnetic form is greater than that of the magnetic, it is found that when the temperature is lowered there is a great and rapid decrease in the resistivity as the alloy passes from the non-magnetic to the magnetic state.

One notable effect was discovered in the case of bismuth. When bismuth wire, at 20°, is placed in a magnetic field so that the wire is tranverse to the direction of the field, its resistance is increased by 6 per cent. If, however, the wire is cooled in liquid air, the increase in resistance, when the wire is placed in a magnetic field, amounts to 368 per cent.

When a metal passes from the liquid to the solid state there is a great decrease of the resistivity, or a great increase of the conductivity. This was well shown by mercury. When solid mercury is slowly heated from −200° there is a slow steady increase of the resistivity up to the melting point. When this is reached there is a sudden and notable increase of the resistivity.

Dewar and Fleming also, assisted as on other occasions by J. E. Petavel, determined the effect of temperature, down to −200°, on the magnetic properties of a number of steels, and an extended investigation of the variation of thermo-electromotive force was also carried out.

The long series of investigations into the electric and magnetic properties of matter at low temperatures opened up a large region of new knowledge. They were regarded as pioneering experiments, the results of which would " serve to broaden those foundations on which we may profitably erect new hypotheses of electric and magnetic phenomena ".

From these studies Dewar and Fleming passed to a study of dielectric constants at low temperatures. Liquid oxygen, it was found, has a very low dielectric constant—1·493 at −182°—this low value being in harmony with the fact that the specific resistance is very large. It was found to obey Maxwell's law that the product of dielectric constant and magnetic permeability is equal to the square of the refractive index for waves of infinite wave-length. The dielectric constants of organic compounds all decrease with fall of temperature. While the presence in the compound of certain groups, such as OH, CO, and CO_2H, leads to high values of the dielectric constant of liquids at the ordinary temperature, this effect is annulled by cooling, the constant falling for all liquids to about

2·5 at −185°. The behaviour of solutions of electrolytes was also investigated.

As early as 1885 Dewar had shown that many reactions which take place with the greatest vigour at ordinary temperatures fail entirely at the low temperatures obtained with liquid oxygen. At −130°, for example, liquid oxygen is without action on phosphorus, sodium, potassium, solid hydrogen sulphide, and solid hydrogen iodide; and liquid ozone is without action on carbon disulphide. Although all chemical change does not cease at low temperatures, it seemed possible that chemical reaction between substances might be so greatly reduced that even fluorine—the most reactive of all the elements—might be manipulated in glass vessels if the temperature were sufficiently reduced.

In 1897, therefore, Dewar, in collaboration with Moissan, who had isolated fluorine in 1886 and who brought his apparatus for the production of gaseous fluorine to the chemical laboratory of the Royal Institution, initiated experiments on the liquefaction of this element and carried out a study of its properties.

When fluorine was passed into a small glass bulb immersed in freshly prepared liquid air at a temperature of −190°, it passed into a clear yellow liquid, which boiled at −187°. No solidification took place even when the temperature was lowered to −200°. The density and other physical properties of the liquid were determined, at least approximately, and a number of experiments on its chemical reactions were carried out. The investigation was resumed in 1903 after hydrogen had been obtained in the liquid state by Dewar, and after Moissan had shown that fluorine, when completely freed from hydrofluoric acid, does not attack glass at the ordinary temperature.

By the use of liquid hydrogen, boiling at −252·5°, fluorine could be not only liquefied but also solidified. The yellow liquid passes into a yellow solid, which on being cooled to −252·5° becomes white —a change in colour which is shown also by chlorine, bromine, sulphur, and a number of other substances. The melting point of fluorine was found to be −233°. Since Dewar and Moissan had found in the earlier experiments that liquid fluorine, even at a temperature of −187°, reacted vigorously with hydrogen and with oil of turpentine, it was of interest to determine whether reaction would still take place when the temperature was reduced to −252·5°. A small quantity of solid fluorine, cooled to the temperature of liquid hydrogen, was brought in contact with that liquid. The result,

described in the *Comptes rendus*, reads: "Une violente explosion s'est produite aussitôt avec mise en liberté d'une quantité de chaleur telle que la matière a été portée à l'incandescence et que l'hydrogène a pris feu. L'explosion a été assez forte pour réduire en poussière le tube de verre et le vase à double paroi qui contenait l'hydrogène liquide."

At $-187°$ liquid fluorine reacted vigorously with sulphur, selenium, phosphorus, and arsenic, decomposed calcium oxide with incandescence, and reacted explosively with anthracene.

During the winter of 1901, Dewar, in collaboration with H. O. Jones at Cambridge, commenced the study of the interesting compound, nickel carbonyl, which had been obtained in 1890 by Ludwig Mond and his co-workers. Not only the physical properties—vapour density and degree of dissociation at different temperatures, critical temperature and pressure, and vapour pressure of the liquid—were investigated, but also the chemical reactions which nickel carbonyl undergoes with other substances. Interest here was directed to the question whether nickel carbonyl could be employed as a synthetic agent. Chlorine and bromine were found to react readily with the carbonyl in chloroform solution; reaction with iodine was relatively slow at the ordinary temperature, so that the velocity of reaction was easily measurable. The aromatic hydrocarbons benzene, toluene, *m*-xylene, and mesitylene were found to react with nickel carbonyl in presence of aluminium chloride, with production of aldehydes and hydrocarbons. Benzene, for example, gave rise to anthracene, and *m*-xylene to 2 : 4-dimethylbenzaldehyde.

The properties of iron pentacarbonyl and of diferrononacarbonyl, similarly, came under investigation, and in the course of their work Dewar and Jones discovered a third iron carbonyl, iron tetracarbonyl, which was best obtained by heating diferrononacarbonyl with toluene in a sealed tube at 95°. The tetracarbonyl was obtained in the form of dark-green, lustrous prisms. In most of the liquids in which the compound is soluble the crystals dissolve to yield solutions of a dark green colour, but solutions in pyridine, and also in alcohol, which are at first green in colour, change quickly to red. Dewar and H. O. Jones were led to conclude that the green coloured compound is a highly polymerised form of $Fe(CO)_4$.

When thiophosgene (thiocarbonyl chloride) was allowed to act on nickel carbonyl at the ordinary temperature, Dewar and H. O. Jones found that a solid polymeric form of carbon monosulphide was

produced, and this polymeride was also formed at temperatures as low as $-20°$. As Sidot had shown that this polymeric compound is produced by the action of light on carbon disulphide, Dewar and Jones sought to prepare the compound and to isolate the monomeric form by *subjecting carbon disulphide vapour*, under reduced pressure, to the action of the silent electric discharge. Evidence of the formation of the monosulphide was obtained; and, when the vapours were passed into a tube immersed in liquid air, a brown substance condensed on the walls of the tube. When the temperature was allowed to rise, the condensed substance underwent change with explosive violence, and a brown solid, similar to the polymeric compound previously obtained, was formed. This polymerisation of carbon monosulphide takes place rapidly at the ordinary temperature even in presence of carbon disulphide vapour.

Attention has already been drawn to the diversity of scientific interests shown by Dewar in the early days of his scientific career, and to the fact that some of his early researches, initiated somewhat tentatively, were taken up again in later years. One of his early interests was in the field of specific heats and other thermal properties. In 1872, at Edinburgh, Dewar, who was at that time interested in calculations of the solar temperature and in the production of high temperatures, carried out a series of determinations of the mean specific heat of carbon, in the form of gas retort carbon, graphite, and diamond, between 1040—2000° and the ordinary temperature. An increase of the specific heat with temperature was found, but the value even at the highest temperature—namely, 0·42—gave a value for the atomic heat which was lower than that required by Dulong and Petit's law.

At a much later date, 1904, Dewar's interest in calorimetry was revived. His mind was now occupied with the investigation of the properties of matter, not at high but at very low temperatures; and he devised ingenious forms of calorimeter, later greatly improved, by means of which the specific heat and latent heat of vaporisation of low-boiling liquids could be determined, as well as the specific heats of solids at low temperatures. In general, the calorimeter consisted of a vacuum vessel filled with liquid air or liquid hydrogen, which was kept from evaporating by being immersed in another vessel of liquid air or hydrogen. The latent heat of vaporisation of the liquid (air or hydrogen) was determined by dropping into the inner vessel a weighed amount of mercury, platinum, silver, etc., and measuring the volume of air or of hydrogen which evaporated

owing to the heat added. To determine the specific heat of the liquid, the pressure on the liquid was reduced to about half an inch of mercury, and mercury was run in until the pressure rose to 1 atm. The heat required to raise the liquid from its boiling point under the pressure of ½ inch to its boiling point under atmospheric pressure could be calculated from the amount of mercury run into the liquid.

During the years 1912 and 1913, these calorimetric methods were improved and applied, more especially, to the determination of the specific and atomic heats of the elements, and the specific and molecular heats of compounds, both inorganic and organic, at temperatures between those of liquid nitrogen (80° K.) and liquid hydrogen (20° K.), or a mean temperature of 50° K. A discussion of the results of a very large number of determinations of specific heat need not be attempted here; but attention must be drawn to one very important discovery which was made by Dewar—namely, that the atomic heat of the solid elements at a mean temperature of 50° K. is a *periodic function of the atomic weight*. When the values of the atomic heat are plotted against the atomic weight of the elements, a graph is obtained which is very similar to the Lothar Meyer atomic volume curve. With regard to the values of the atomic heat, Dewar remarked: "If experiments were similarly made between the boiling points of hydrogen and helium, then in all probability the atomic specific heats would be all very small and nearly constant. Until more accurate values of the atomic heats have been reached by the use of purer samples of the elements and the latest form of this calorimeter, it will be advisable to delay theoretical discussion." Although a number of determinations of the specific heats of elements and compounds were later made with the improved calorimeter, the results of which are summarised in the volumes of Dewar's "Collected Works", no theoretical discussion of his previous results was ever published.

Owing to the conditions produced by the outbreak of war in 1914, Dewar found it impossible to continue his researches at low temperatures; and, as it was not till a later period of the war that he was called upon to apply his exceptional knowledge and experience to the development of metal vacuum-jacketed containers for liquid oxygen for use by air-pilots, he had to seek solace and satisfaction for his restless, questing mind in other directions.

Diffusion of gases through various septa first captured his interest, and he studied the diffusion of various gases through iron, platinum,

and quartz glass at high temperatures. He also extended Graham's investigation of the diffusion of gases through thin rubber membranes, and found that at 15° the relative rates of diffusion (air being put equal to 1), were: nitrogen, 0·69; argon, 1·28; helium, 1·75; oxygen, 2·0; hydrogen, 5·6; carbon dioxide, 14·0. The relative rates, however, vary somewhat with the temperature.

The study of gaseous diffusion through thin rubber membranes led to the examination of other films of great tenuity, solid films produced by the evaporation of solvent from amyl acetate solutions of nitrated cotton, and liquid films obtained with Plateau's soap solution. Soap bubbles and soap films had interested Dewar at an early period, and he had made them the subject of his first Christmas Course of lectures to a juvenile auditory in 1878–79; and in the early years of the war, Dewar, again attracted by them, studied, as the pure experimentalist, the production and behaviour of single bubbles, chains and clusters of bubbles, and the complicated geometrical systems of films formed on wire frames. The life of soap bubbles, Dewar found, is dependent mainly on the freedom from deleterious gases—especially carbon dioxide—and from solid particles of the atmosphere in which they are blown. Large bubbles—up to 46 cm. in diameter—were produced and preserved for three months or more. A great bubble, 4 feet in diameter was blown in a cool, cement-lined cellar, but in spite of all attempts to obtain an atmosphere free from particles, these bubbles did not last more than a few hours.

Dewar's experiments with soap films, however, had a purpose other than the purely philosophical. A soap film was formed across a constriction in a sealed, exhausted tube, which contained also a supply of the soap solution. This soap film had very great stability and when first formed showed the usual interference colours. Very soon, however, the upper portion of the film cleared and became black, leaving a lower coloured section with a sharply defined, horizontal edge. When the tube was tilted, the coloured section immediately responded to the motion so that the upper edge of the coloured band remained horizontal. The film could thus be used as a level; and Dewar hoped that it might be found useful by air-pilots to show when their plane was on "an even keel". Although it was not found suitable for this purpose, it may be that, in other circumstances, such a level, rapidly responding and free from lag and unsteadiness, will be of value.

Down almost to the day of his death, Dewar was engaged in the

study of soap films—the rate of development of black films, the great variety of streaming patterns which are formed by the impact of jets of air on the films, the distortions produced by different sounds, etc.—and the description of the varied behaviour shown, illustrated by numerous photographs, makes fascinating reading, and fills one with admiration of his imaginative ability in devising the experiments and of his extraordinary skill as an experimentalist.

In 1906, Dewar had found that a workable thermoscope could be constructed by taking advantage of the fact that charcoal, saturated with air or other gas at a low temperature, is very sensitive to the energy of radiation, and that the small rise of temperature produced in a 1-gram bulb of charcoal by the approach of a candle flame expels sufficient gas to move a suitable index. At first, the charcoal was contained in a glass bulb, but, since a thin membrane of stretched rubber is more transparent than glass to heat, the sensitivity of the thermoscope can be increased by enclosing the charcoal in a metal capsule covered with a thin clear rubber membrane. This membrane, as Dewar had previously shown, is practically impermeable to most gases at low temperatures.

With this thermoscope, Dewar was able to measure the transmissive power for infra-red radiation up to 100° of a large number of materials when immersed in the form of plates of various thicknesses in the liquid air above the cell. The paraffins and benzene exhibit high transmissive power, and halogen substitution generally increases the value. A greater power of transmission is shown by esters and by pyridine and its associates; but alcohols, ketones, acids, amides, etc. absorb infra-red radiation.

The relative emissivities, also, of a number of metals, in the form of polished plates, were also determined by means of the thermoscope, the following values at 100° being obtained:

"Black body" ...	100	Aluminium	9	Copper	5
Iron	14	Zinc	7	Brass	5
Lead	14	Nickel silver ...	6	Mercury	3
Tin	12	Pewter	5		

In 1872, in Edinburgh, Dewar had interested himself in the calculation of solar temperature, and in the closing years of his life he applied an ingeniously designed modification of his original thermoscope to the measurement of the radiation from the sky, both by day and by night, from the sun during partial eclipse, from the moon, and from clouds. The thermoscope was erected immediately under a sliding skylight in one of the laboratories of the Royal

Institution, and there, in this improvised observatory, Dewar, now nearly 80 years of age, kept vigil with the stars, observing and recording the varying radiation through various sequences of weather conditions. This work, an account of which may be read in the *Proceedings* of the Royal Institution or in Dewar's " Collected Works ", is a tribute not only to his patience and abiding interest in the advancement of science but also to his wonderfully refined manipulative skill.

HENRY EDWARD ARMSTRONG

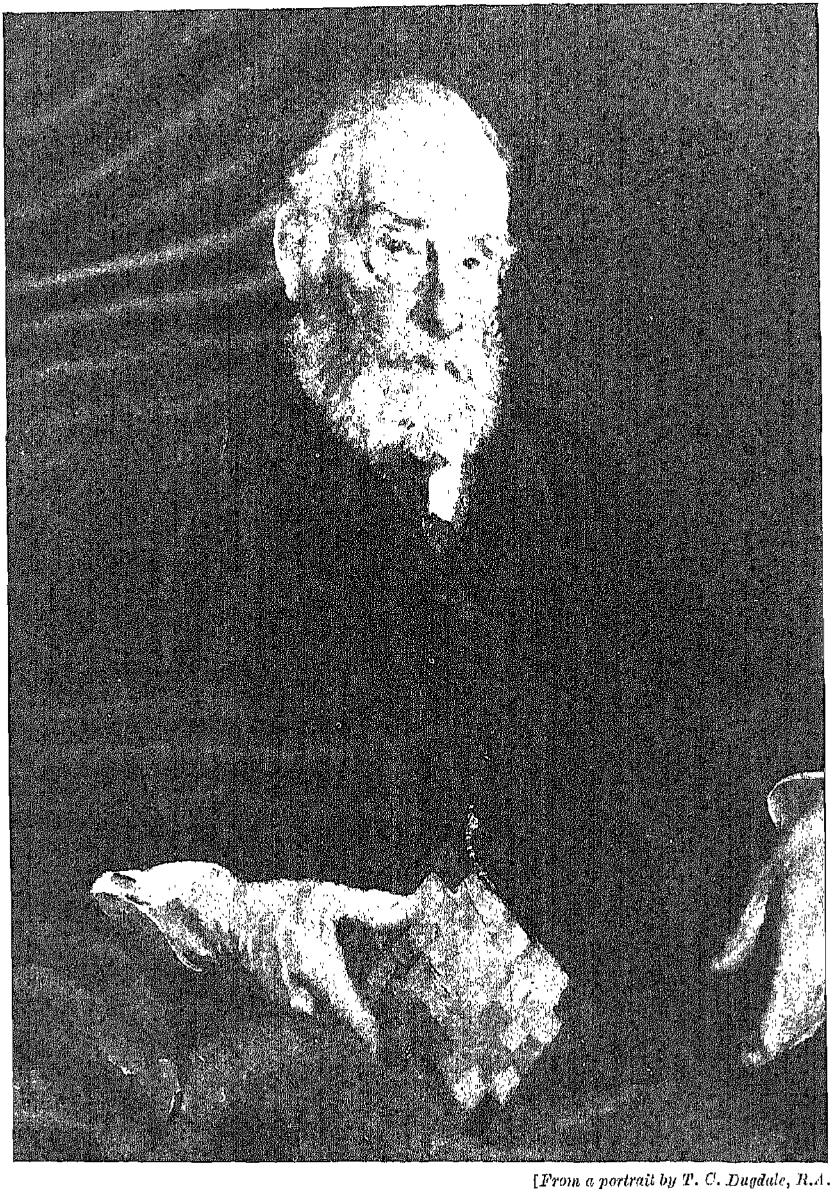
1848—1937

HENRY EDWARD ARMSTRONG died on July 13th, 1937, in his ninetieth year. By his death British chemical science lost its most outstanding personality, one who by his vigorous mind, independent outlook, and rare gift of expression both in speech and in writing had a profound influence on the development of chemistry during two generations. In his prime he was probably the most constant attendant, the most frequent and vigorous speaker, at the meetings of the Chemical Society. Like many men of quick brain, he was often impatient, not suffering fools gladly, but criticising freely; a thorn in the flesh to many, but generous in his appreciation of good work. Unorthodox and critical, he would never bow the knee to authority, however eminent, if his reason went against the popular view. Consequently his life was full of controversy, which he thoroughly enjoyed. Few men have lived a fuller life than he, or retained a mind as unclouded as his was to the end of nearly ninety years.

Armstrong's services to the Chemical Society were unique. He was secretary for eighteen years from 1875 to 1893, and during that period he appears to have ruled the Society with a rod of iron. From 1893 to 1895 he was President, following Crum Brown, and from then until his death, with two short breaks, was Vice-President. He first served on the Council in 1873, when he was but twenty-five years old, and from that date until his death was a member of Council almost continuously.

Armstrong was born on May 6th, 1848, at Avenue Road, Lewisham, and lived in Lewisham all his life. A year before his death, feeling that the end was near, he wrote a short autobiography, reproduced in the issue of *The Central* * of June, 1938, from which some of the following particulars are taken. His father, Richard Armstrong, was a commission agent and importer of Mark Lane, a man of

* The Journal of the Old Students of the City and Guilds (Engineering) College, formerly the Central Technical College.



[From a portrait by T. C. Dugdale, R.A.

H. E. ARMSTRONG

kindly disposition, amiable almost to excess. His paternal grandfather, another Richard Armstrong, one time Governor of the Convict Prison of Gibraltar, was a man of most irascible disposition, with a strong objection to tobacco. Henry Edward, who also hated tobacco smoke, inherited some of his grandfather's characteristics.

Of his early years Armstrong had little recollection, he says, but his mind retained a picture of the countryside in which he played as a boy, of rivers, chalk-pits, and ponds, and the beginnings of an interest in entomology and geology which stayed with him throughout his life. After attending small schools, he passed to the Colfe Grammar School, Dartmouth Hill, and his school career finished when he left there in 1864 at the age of sixteen, conscious, as he says, of no particular interest, but observant and an experimentalist. A book which he discovered at school had a permanent influence on his mind. This was Trench's "Theory of Words", which held him fascinated, and made him critical of meanings. This confession is illuminating to those who knew him in later years as a connoisseur of language and the stern critic of those who dared to misuse it. He was once criticised publicly for splitting an infinitive in a letter to *The Times*, and he never forgot it. He was always ready to learn.

At the time of leaving school Armstrong was supposed to be delicate, and he spent the following winter at Gibraltar with his uncle; it was here that he saw the first British steam-driven iron-clad, the *Warrior*. On his return in the spring of 1865 to London he entered, for no apparent reason, at the Royal College of Chemistry in Oxford Street, and so "just slid into chemistry". He was just in time to attend the College whilst A. W. Hofmann was still there; almost at once Hofmann left for Berlin, and Edward Frankland succeeded him. Chemical training in those days was not lengthy. Perkin, as is well known, left the Royal College of Chemistry at nineteen to become a dyestuff manufacturer; Horace Brown, Armstrong's most intimate friend, left at seventeen and a half after six months training to become a famous brewing chemist; and Armstrong himself, after a year and a term, was picked by Frankland to assist him in research. He would then have been just eighteen years of age.

This first research with Frankland was one in which he, in after years, always took great pride. Frankland had been appointed one of three members of a Royal Commission directed to inquire into the pollution of rivers and the domestic water supply of Great Britain. Armstrong's task was to devise methods for determining

the organic impurity in sewage and of sewage matter in drinking-waters. Frankland gave his assistant the minimum amount of instructions, and as a result Armstrong acquired confidence as an independent worker. The method they devised for water analysis by combustion in a vacuum was used by Frankland between 1868 and 1872 for surveying the whole British water supply, and as a result of his work typhoid fever became a preventable disease, and this country soon led the world in the provision of safe domestic water.

Armstrong had a great admiration for Frankland, and in his Frankland Memorial Oration to the Lancastrian Frankland Society, delivered in 1934, has left us an intimate study of his career and of those with whom he was associated. Frankland had, as is well known, worked with Kolbe in Marburg; it was, in fact, at Marburg in Bunsen's laboratory that he discovered the zinc alkyls, which were of great importance in the development of his ideas of valency. Nothing was more natural, therefore, than that Frankland should recommend young Armstrong to go and study under Kolbe, then Professor of Chemistry at Leipzig. To Leipzig Armstrong went in October, 1867, staying there for five happy semesters. Here he had his introduction to aromatic chemistry; he had not even heard of Kekulé's benzene formula when he arrived. Kolbe introduced him to sulphonic acids, a class of compound for which he acquired a life-long affection. Kolbe must have been cast in a mould similar to Armstrong's own, or perhaps the pupil copied the master, for in later years Armstrong wrote of Kolbe the following words which might apply equally to himself: " . . . a chemist who received but scant justice from his own countrymen . . . because he dared to criticise and expressed himself in the biting terms of a clear and concise diction, in a pure German which no one else in those days had at his command; in fact, he took his countrymen greatly to task for their slovenly language ". It was characteristic of Armstrong's industry that, on arriving in Germany, he should at once begin to accumulate books—a set of the *Annalen*, from which he translated many papers in order to master the language and learn to read *with attention* (his own words), and copies of Goethe, Schiller, and Lessing.

His degree of Ph.D. was gained in 1869 for a thesis, the gist of which was published in the *Proceedings of the Royal Society* (1870, **18**, 502) under the title " Contributions to the History of the Acids of the Sulphur Series, I. On the Action of Sulphuric Anhydride on

Several Chlorine and Sulphur Compounds," communicated to the Society by Frankland. In this early paper his characteristic way of challenging authority shows up. Referring to a statement in the literature that carbon disulphide and sulphuric anhydride are without action on one another, he says: "Notwithstanding this, I thought it advisable to repeat the experiment, and have by so doing found a reaction take place exactly in the sense I had expected." He found, in fact, that carbonyl sulphide was formed according to the equation $CS_2 + SO_3 = COS + SO_2 + S$. He also discovered the formation of pyrosulphuryl chloride by the action of sulphuric anhydride on carbon tetrachloride: $CCl_4 + 2SO_3 = COCl_2 + S_2O_5Cl_2$.

On returning to London, Armstrong obtained a post at the Medical School of St. Bartholomew's Hospital, under Dr. Matthiessen, taking charge of special classes in chemistry for students proceeding to the London degree; here he worked with Matthiessen on alkaloids until the latter died in October, 1870. His association with the medical students continued for about twelve years. Another post came to him in 1871 when he was appointed Professor of Chemistry at the London Institution, Finsbury Circus. His duties were to instruct students in analytical chemistry and the methods of original investigation, from 6 to 8 p.m. If the duties were light, so was the professional salary, £50 a year, without any laboratory allowance. But he had a private laboratory, though it was little more than a coal-hole, so close to the lecture theatre that the disagreeable odours from his investigations of the higher-boiling constituents of coal tar were a source of considerable discomfort to the audience in the theatre. Writing of this period, Armstrong has said: "As the fees derived from the London University classes were small—never equal to my professional pay—to supplement my income I did sundry odd jobs, including examination work, but never strove to be a consultant. I thus led an erratic but varied and happy existence and had many opportunities of gaining experience beyond those of an assistant in any of the big laboratories of to-day. Living under such conditions, a critic from my youth, I could not but grow up a free-lance and an iconoclast—even a thorn in the side of my superior colleagues when I ventured to differ. It was an age of discussion—we were not fully persuaded even to believe in atoms." How many men, however, under such conditions, would have developed into the force Armstrong became? It was his enquiring mind and unquenchable energy which carried him forward.

A former Professor at the London Institution had been Grove, the inventor of the unpolarisable Grove cell. Some of his apparatus still remained in the laboratory. Armstrong studied this apparatus, bought at an auction some copies of the Royal Society's *Transactions* containing Grove's memoirs, and from reading them became electrolytically minded. This circumstance influenced Armstrong's views on chemical change throughout his life. He also extended his reading and his income at this time by becoming, in 1871, an abstractor for the Chemical Society under Henry Watts.

The seventies were for Armstrong comparatively uneventful years; he was preparing for his life's work, learning what was required of a teacher and of a student; feeling his way in research; filling his retentive mind with facts; learning to write and to manage men. During this period he wrote an "Introduction to Organic Chemistry", published in 1874. This task, he says, put system into his soul but not much money into his purse. He also wrote the inorganic section on "Chemistry" for the ninth edition of the "Encyclopædia Britannica", published in 1876, and was probably the first to base an account of inorganic chemistry on Mendeléef's generalisation. With C. E. Groves he produced a new edition of Miller's "Organic Chemistry", published in 1880, almost entirely rewritten. These undertakings, and his habit of reading current chemical literature as soon as it appeared, gave him that wide knowledge which he so often and so aptly displayed in discussions at scientific meetings. It is remarkable, and worthy of serious consideration, that Armstrong himself considered that the development of his critical faculty was notably influenced by his experience of law cases. In 1879 he took part in the action for infringement of Kolbe's salicylic acid patent brought by von Heyden against Neustadt, and he describes this experience as the coping stone of his education in scientific method. "The display of judicial method, the stringent examination and cross-examination of every particular, came to me as the acme of scientific treatment; I realised how far short we were from it in our ordinary treatment of our problems; it made me the unpleasant critic I have since been."

Armstrong's life work started when, in October, 1879, at the age of thirty-one, he was appointed by the City and Guilds of London Institute for the Advancement of Technical Education, along with W. E. Ayrton, to organise classes in chemistry and physics in temporary premises in Cowper Street, Finsbury. It must be realised that technical education, or the teaching of science with special

reference to its practical applications, was at that time almost non-existent in this country, although since the great Exhibition of 1851 the urgent need for this type of education had been realised. A definite decision was taken by the City Livery Companies of London in 1876 at a meeting at the Mansion House to devote their attention to the promotion of education throughout the country, and especially technical education. The City and Guilds of London Institute was established in 1878 and incorporated in 1880. The appointment of Armstrong and Ayrton in 1879 was for the purpose of carrying out one of the objects of the Institute, the establishment of local schools for artisans and workmen, but the success of their classes soon made it evident that a specially adapted building would be required for their development, in addition to the intended Central Institution for advanced education. Out of this need arose Finsbury Technical College, the first institution of the kind in London, the foundation stone of which was laid in May, 1881. The Central Institution, later known as the Central Technical College, was, however, the principal objective which the City and Guilds of London Institute had in view, and they utilised the services of Armstrong and Ayrton to the full in drawing up their plans for this College. It had been recognised that when these two men were appointed at Cowper Street they were in charge of an experiment, *to ascertain by trial how their subjects could most usefully be taught.* It is from this time that Armstrong's great interest in the technique of education is to be dated, an interest that never wavered during the rest of his life. During the autumn of 1881 he went with Ayrton on a tour in Germany to study there the equipment of the chemical and physical laboratories, at the expense of the City and Guilds of London Institute. When the Central Institution in Exhibition Road, South Kensington, was eventually opened in 1884 by the Prince of Wales, Armstrong went there as Professor of Chemistry. After some hesitation Ayrton accepted the chair of Physics, the other two Professors being W. C. Unwin (Engineering) and O. Henrici (Mathematics). The physics appointment was offered to Oliver Lodge; had he accepted, the course of scientific research at the Central might have run on different lines, for Armstrong has put it on record that he and Lodge had many interests in common. Armstrong held his post at the Central until his compulsory retirement when the College became part of the Imperial College of Science and Technology in 1911 and the Chemical Department was closed. The final dispersion of his students took place in 1914. Thereafter

he became in fact what he had always been at heart, a free-lance; a critic and commentator on affairs and the genial mentor with whom chemists of this generation were so familiar. The loss of his chemistry school and of the opportunity for directly inspiring experimental work was a blow to him. He did not let it depress him, but carried on courageously for nearly a quarter of a century of active mental life.

Armstrong's work falls naturally under three headings, chemical research, education, and activities which may be classed under the general term " affairs ". He was a man who had to have a finger in many pies. This trait must have revealed itself at an early date, for, when he was appointed to the Central, W. A. Tilden, writing to congratulate him, advised him to " concentrate on this work and not try to keep so many things going at once. There is plenty of room for a school of chemistry, and here is your opportunity; but it will take some doing." The advice was utterly wasted, and " affairs " always loomed large in his life; but it must be added that they generally had a close connection with either chemistry or education. This memoir must concentrate more particularly on Armstrong's contributions to chemistry through his researches.

Naphthalene Research.

Armstrong's most substantial contribution to chemistry was the study which he initiated of the laws of substitution in the hydrocarbon naphthalene. He published an isolated paper in 1874 dealing with naphthyl sulphides, but the real start of the work is found in a paper published, partly with Graham, in 1881 (*J.*, 1881, **39**, 138). From this time until 1900 the work was continued, being described in some sixty papers, mostly very brief, appearing in the *Proceedings* of the Chemical Society. When the work started, naphthalene was very much " in the air ". The chemists of the dyestuff firms, particularly in Germany, were just beginning to discover the potentialities of naphthalene derivatives for manufacturing azo-dyes. The two β-naphtholdisulphonic acids known as G and R were first used in 1878 for making respectively yellow (Gelb) and red (Rot) dyes by coupling with diazotised aniline and *m*-xylidine; Read Holliday and Sons in Huddersfield discovered Para Red (from diazotised *p*-nitroaniline and β-naphthol) in 1880; Congo Red, from tetrazotised benzidine and naphthionic acid, was

discovered by Böttiger in 1884. A large number of amines and phenolic compounds and their sulphonic acids were being prepared from naphthalene by empirical methods, but their orientation was unknown and the elucidation of their structure was a matter of great difficulty. The researches of Armstrong and his collaborators contributed in a very large degree—more, it is safe to say, than those of any other group of workers—to the establishment of naphthalene chemistry on a sure basis, and were of inestimable value to dyestuff technologists. Among the collaborators were Amphlett, Davis, Graham, Houlding, Heller, Jenks, Rossiter, Lapworth, Percival, Shelton, Sindall, Streatfeild, Williamson, and, most important of all, W. P. Wynne, whose skill and determination over a period of many years carried the work forward. It seems highly probable that the choice of this subject for his major research may have been made by Armstrong in part at least on account of its technical importance, for at the time of its commencement he was profoundly occupied with the development of schemes for the technical education of young men for industry, and in his view research must always have an important rôle in such schemes.

Armstrong's attention was first drawn to the problem of the constitution of the naphthalenedisulphonic acids when writing an article on naphthalene for a supplement to Watts's "Dictionary of Chemistry" in 1879. Ebert and Merz had shown (*Ber.*, 1876, **9**, 592 *) that by the action of excess of concentrated sulphuric acid on naphthalene at 160—180° two isomeric disulphonic acids were formed, α and β. The α-acid on fusion with caustic potash gave a dihydroxynaphthalene, m. p. 186°, whereas the β-acid gave no dihydroxy-compound but a hydroxysulphonic acid which was suspected of being identical with Schaeffer's acid obtained by sulphonating β-naphthol (now known to be 2 : 6). Armstrong and Graham repeated the work and confirmed the identity of the hydroxysulphonic acid from the β-acid of Ebert and Merz with Schaeffer's acid; they also showed that the β-acid could be fused, with ease, to give a dihydroxynaphthalene; in fact two products were obtained. The disulphonic acid, which gave more soluble calcium salts than the β-acid, and should have corresponded with the α-acid of Ebert and Merz, gave, however, a different dihydroxynaphthalene, and it became evident that there were more than two disulphonic acids. In the paper describing this work Armstrong

* This reference was wrongly given by Armstrong as *Ber.*, **10**, 592, and the mistake has several times been copied.

suggested that Schaeffer's acid might be the 2 : 3-compound, but he was admittedly speculating with insufficient evidence.

The difficulty of separating mixtures of sulphonic acids led Armstrong, in his first work with Wynne, to apply to naphthalene a much milder sulphonating agent, chlorosulphonic acid, with which he had already had experience in sulphonating narcotine and codeine, in the hope that a single product might be obtained. This expectation was realised. Working in carbon disulphide solution, with one molecular proportion of chlorosulphonic acid, only the α-monosulphonic acid was obtained; with slightly more than two molecular proportions a new disulphonic acid was formed, which was correctly inferred to be the $\alpha^1\alpha^{4'}$-modification (in modern nomenclature 1 : 5). When potassium β-naphthalenesulphonate was warmed with excess of chlorosulphonic acid still another new disulphonic acid was obtained (the 1 : 6-isomeride). Simultaneously, work was carried out on the action of bromine on naphthalenesulphonic acids and on Schaeffer's acid, resulting in the preparation of brominated naphthaquinonesulphonic acids and the discovery that α-sulphonic groups are readily displaced by bromine, but β-sulphonic groups only when the ring undergoes oxidation. Schaeffer's acid gave a bromohydroxynaphthaquinonesulphonate and a dibromohydroxynaphthaquinone. The action of chlorosulphonic acid on α-nitro-, -chloro-, and -bromo-naphthalene was also studied. Whilst α-nitronaphthalene gave only the 1 : 5-acid, α-chloro- and -bromo-naphthalene gave mainly the 4-sulphonic acids and in addition small amounts of an isomeric acid. The β-chloro-, -bromo-, and -iodo-naphthalenes each gave two isomeric acids with chlorosulphonic acid (*Proc.*, 1887, **3**, 22).

To make it possible to ascertain the orientation of the numerous derivatives of naphthalene which were being discovered it was necessary to have a series of reference compounds of known constitution which could be readily identified. To this task Armstrong set himself, and he chose as the reference compounds the dichloro- and trichloro-naphthalenes. It had been observed by Cleve in 1876 that when a naphthalenesulphonyl chloride is distilled with phosphorus pentachloride it is converted into the corresponding chloronaphthalene; and that β-naphthol when treated in the same way gives β-chloronaphthalene. Armstrong announced in 1882 (*Ber.*, 1882, **5**, 200) that he was using this as a diagnostic method, and with Wynne he developed it. It was shown that bromo- and nitro-substituents were also displaced by chlorine when compounds

containing them were distilled with phosphorus pentachloride. As further reference compounds the chloro-substituted mono- and di-sulphonyl chlorides were prepared. Naphtholsulphonates were converted into chloronaphthalenesulphonyl chlorides by the action of phosphorus pentachloride at a moderate temperature; and naphthylaminesulphonic acids were converted into chlorosulphonic acids by Sandmeyer's method, which was given much study, whilst as an additional precaution, especially with naphthylaminedisulphonic acids, the amino-group was eliminated and the naphthalenedisulphonic acid obtained was converted into the corresponding dichloronaphthalene. In 1895, when the work was nearing completion, Armstrong and Wynne published results justifying the use of the phosphorus pentachloride method of converting sulphonyl chlorides into chloronaphthalenes (*Proc.*, 1895, **11**, 83). They showed that the reaction takes place when the sulphonyl chloride is heated in the absence of phosphorus pentachloride, albeit the yield of chloronaphthalene is not so good, probably because a higher temperature is necessary. When phosphorus pentachloride is used there may take place some additional chlorination; thus a chloronaphthalenedisulphonyl chloride may give rise to some tetrachloronaphthalene in addition to the trichloronaphthalene which is the main product. This circumstance was a source of error by another worker on at least one occasion.

In later work the conversion of 6- and 7-chloronaphthalene-1 : 3-disulphonyl chlorides into trichloronaphthalenes by heating with phosphorus pentachloride was studied in detail and it was shown that intermediate dichloro-monosulphonyl chlorides were formed without change of orientation (*Proc.*, 1897, **13**, 152). One unexpected change of orientation was discovered, however, when 1 : 8-dichloronaphthalene-3-sulphonic acid was heated with acids under certain conditions; instead of the expected 1 : 8-dichloronaphthalene, the 1 : 5-isomeride, and, under one set of conditions, the 1 : 7-compound was obtained. When 1 : 8-dichloronaphthalene was heated with concentrated hydrochloric acid at 290°, it was entirely converted into the 1 : 5-compound. These isomeric changes might repay further study.

The characterisation of the ten theoretically possible dichloronaphthalenes deducible from the Erlenmeyer formula for naphthalene was finally completed by Armstrong and Wynne in 1890 (*Proc.*, 1890, **6**, 77). Twelve had actually been described and it was clear that two at least of these were superfluous. The twelve

are included in the following table, in order of ascending m. p.; the Greek letters by which they were known are given, and their finally established orientation, according to modern numbering.

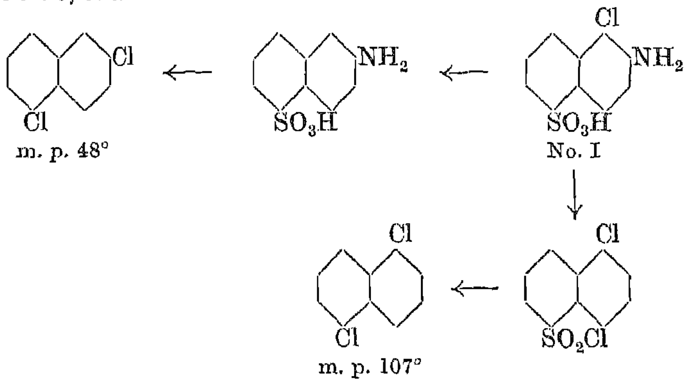
No.	Designation in 1888.	M. p. in 1888.	Corrected m. p., Armstrong and Wynne.	Orientations.	No.	Designation in 1888.	M. p. in 1888.	Corrected m. p., Armstrong and Wynne.	Orientations.
1	—	34°	35°	1 : 2	7	ζ	83°	82°	1 : 8
2	α	38	—	—	8	κ	94	—	—
3	η	48	48	1 : 6	9	γ	107	106·5	1 : 5
4	θ	61·5	61	1 : 3	10	δ	114	114	2 : 7
5	θ'	65	62·5	1 : 7	11	ι	120	119·5	2 : 3
6	β	68	67·5	1 : 4	12	ε	135	135	2 : 6

Of these compounds the three $\alpha\alpha$-compounds, Nos. 6, 7, and 9, and the two heteronuclear $\beta\beta$-compounds, Nos. 10 and 12, were known with certainty by 1888. In that year Armstrong and Wynne published a paper (*Proc.*, 1888, 4, 104) describing an investigation of the $\alpha\beta$-compounds. They showed that the so-called α-compound (No. 2) obtained by heating naphthalene tetrachloride with potash (curiously, this was the first ever described) is a mixture, and must therefore be removed from the table. When sulphonated, it gave two sulphonic acids which, when separated and reconverted into dichloronaphthalenes by hydrolysis, gave two compounds, m. p. 68° and 61·5°. The former is the 1 : 4-compound, and as the only $\alpha\beta$-dichloronaphthalene which can be expected from naphthalene tetrachloride is the 1 : 3, the orientation of that of m. p. 61·5°, θ in the table, is 1 : 3. It was further shown that different workers had confused two dichloronaphthalenes of approximately the same m. p., about 61°. The second, which could be obtained from the Badische β-naphthylaminesulphonic acid, had a rather higher melting point, 64° (later corrected to 62·5°; θ' in the table). No. 1 in the table, m. p. 34°, being homonuclear, must be 1 : 2 by exclusion. Of the $\alpha\beta$-compounds, therefore, either η, m. p. 48°, or θ', m. p. 62·5°, must be 1 : 6 and the other 1 : 7. This question was settled by studying the sulphonation of 1-chloro-2-naphthylamine. One of the three sulphonic acids thus obtained was diazotised to remove the amino-group, and the resulting chloronaphthalenesulphonic acid converted into the dichloronaphthalene, which had m. p. 107° and must be the 1 : 5. This settled the position of the sulphonic group. The same chloronaphthylaminesulphonic acid was then reduced to remove the chlorine, and the amino-group replaced by chlorine; the chloronaphthalenesulphonic acid gave by the standard method the dichloronaphthalene of m. p. 48°. This set of experiments settled that the dichloronaphthalene of m. p. 48° (η) is 2 : 5,

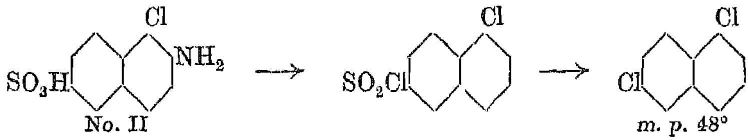
i.e., 1 : 6; the other of m. p. 62·5° (θ′) must therefore be 1 : 7. The same conclusion had been arrived at by Erdmann and Kirchoff, who had synthesised a dichloronaphthalene by condensing *p*-chlorobenzaldehyde with succinic acid, cyclising the resulting chlorophenylparaconic acid into chloronaphthol, and converting this into dichloronaphthalene, which had m. p. 61·5°. Armstrong, however, did not at this time trust the synthetic method, though he later admitted its value.

There remained two compounds of the table to be disposed of, No. 8 (κ) and No. 11 (ι). No. 8, which had been obtained by Claus from sulphonated α-naphthol, was shown to be 1 : 2 : 4-trichloronaphthalene, and goes out of the table. No. 11 was proved in 1890 to be the 2 : 3-compound by its preparation from 1 : 2 : 3-trichloronaphthalene by partial reduction.

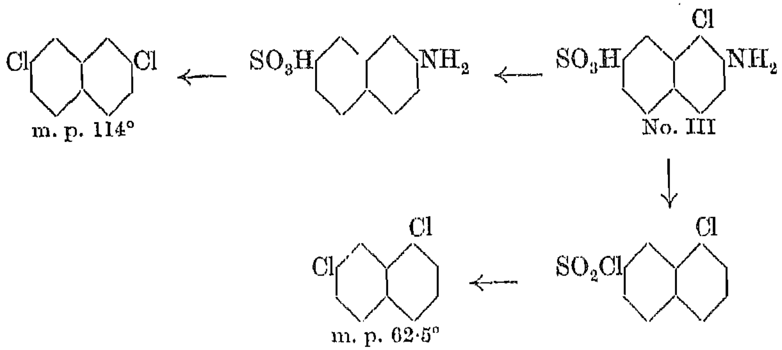
In such a manner the ten dichloronaphthalenes were identified. It will be understood that many cross-checks were provided in the course of the work. As an example, it has been stated that 1-chloro-β-naphthylamine gave three different acids on sulphonation. No. I has been shown to be the 5-sulphonic acid, since from it was prepared 1 : 5-dichloronaphthalene besides the η compound, shown to be 1 : 6, thus:



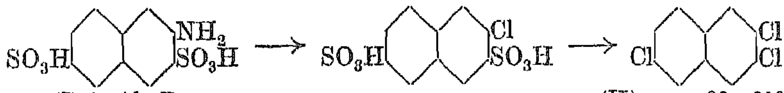
The second acid, No. II, was also converted into a dichloronaphthalene, m. p. 48°, after elimination of the amino-group, and must therefore be 1 : 2 : 6:



Finally the third acid gave, by appropriate methods, a dichloronaphthalene, m. p. 114°, known to be 2 : 7, and one of m. p. 62·5°, already shown by exclusion to be 1 : 7, a conclusion now doubly confirmed, since No. III must have the 1 : 2 : 7-configuration :



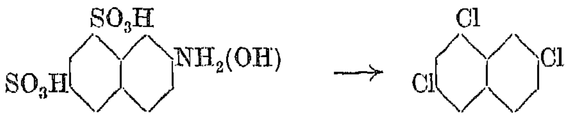
In 1889 Armstrong and Wynne started a systematic study of the tri-derivatives of naphthalene, and in the opening paper of the series (*Proc.*, 1890, 6, 11) the technical importance of the project was emphasised, particularly the need for knowing the constitution of the isomeric naphthol- and naphthylamine-mono- and -di-sulphonic acids, which showed such striking differences in their behaviour with diazo-compounds and in the colour and other properties of the azo-dyes derived from them. The work on the dichloronaphthalenes had been crowned by studying the sulphonation of each with chlorosulphonic acid in carbon disulphide solution and preparing the derived sulphonyl chlorides; in the case of the trichloronaphthalenes, fourteen of which were predicted by theory, which were to serve as reference compounds for the tri-derivatives, it was pointed out that it was still more necessary to characterise each compound, owing to the close similarity between the isomerides; no fewer than four melted at nearly the same temperature, 90—92°. It will be impossible to refer to more than a small part of the work accomplished by Armstrong and Wynne in the course of their search for the trichloronaphthalenes. One can illustrate what was accomplished by reference to the work on the two naphthylaminedisulphonic acids R and G, which were supplied by the Aktiengesellschaft für Anilinfabrikation and by F. Bayer and Co. The R acid gave, after elimination of the amino-group, the 2 : 7-disulphonic acid of Ebert and Merz. The amino-acid could therefore only have the constitution (I).



(I) Amido-R (II) m. p. 90—91°

By the standard method it was converted into the trichloronaphthalene (II), m. p. 90—91°, which must be the 2 : 3 : 6.

The so-called amido-G acid gave, after elimination of the amino-group, a new naphthalenedisulphonic acid, the third to be discovered by Armstrong, which gave by the standard method the known 1 : 3-dichloronaphthalene. This settled the relative positions of the two sulphonic groups. Now it was known that the hydroxy-G acid corresponding with amido-G was obtainable by further sulphonating Bayer's β-naphtholsulphonic acid (2 : 8); further it was stated by Caro and confirmed by Armstrong and Wynne that the hydroxy-G acid when reduced by sodium amalgam lost one sulphonic group and gave Schaeffer's β-naphtholsulphonic acid (2 : 6). It follows that both amido-G and hydroxy-G acids must have the 2 : 6 : 8-configuration (III).



(III) Amido- and hydroxy-G m. p. 113°

The corresponding trichloronaphthalene had m. p. 113°; this compound had already been obtained by Alén from a nitro-acid by nitrating Ebert and Merz's naphthalene-β-disulphonic acid (2 : 6); the nitro-acid must therefore also be the 8-nitronaphthalene-2 : 6-disulphonic acid.

As a result of this work Armstrong concluded that it was the presence of the sulphonic acid group in the 8-position which caused Bayer's acid (2 : 8) and hydroxy-G acid to couple so sluggishly with diazo-compounds, and prevented the corresponding amino-acids from coupling at all, an explanation which is still accepted by dyestuff chemists.

All but one of the fourteen trichloronaphthalenes were known by the end of 1890. The missing one, the 1 : 2 : 8-isomer, was eventually obtained by the synthetic method already referred to. By this method Erdmann and Schwechten had obtained from 3 : 4-dichlorobenzaldehyde two isomeric dichloronaphthols, one of which must be 7 : 8- and the other 6 : 7-dichloro-2-naphthol. Armstrong and Wynne prepared them on a large scale and converted them into the

two trichloronaphthalenes; the dichloro-α-naphthol of m. p. 151° gave the known 1 : 6 : 7-trichloronaphthalene, m. p. 109°; the other, m. p. 95°, gave a new trichloronaphthalene, m. p. 83°, which must be 1 : 2 : 8. Its identity was further confirmed by synthesising it from 2-chloro-1-nitronaphthalene-8-sulphonyl chloride as described by Cleve in 1893. By 1895 Armstrong and Wynne had prepared all the 14 trichloronaphthalenes in quantities of 35—50 grams and had started on the task of further characterising them by preparing from each a monosulphonic acid. Their constitution had, moreover, been determined by so many methods that there was no doubt that the fourteen predicted by theory, and no more, were known. It is worth while to reproduce the following table, given by Armstrong and Wynne (*Proc.*, 1895, 11, 85), which shows how rapidly the scanty knowledge of these compounds which chemists had in 1888 was made complete by 1895. The table shows in the last column how many independent checks were made of the constitution of each compound.

				Constitution and m. p. assigned by				
							Armstrong and Wynne, 1895.	
State of knowledge at end of 1888.		M. p.		Armstrong and Wynne, 1889—1890.		Cleve, 1892—1893.	M. p.	No. of methods used.
α	1 : 2 : 3	81°	Widman	1 : 2 : 3	81°	—	81°	2
	1 : 2 : 4	92	Cleve	1 : 2 : 4	92	—	92	1
			—	1 : 2 : 5	78·5	77, 76°	78·5	5
	? : 2 : 6	91	Forsling	1 : 2 : 6	92·5	90	92·5	4
			—	1 : 2 : 7	83—84	75·5	88 and 84	3
			—	1 : 2 : 8	—	83	83·5	2
γ	1 : 3 : ?	103	Widman	1 : 3 : 5	103	103	103	5
θ	α : 3 : 7	75·5	Alén	1 : 3 : 6	80·5	—	80·5	6
η	α : 3 : 6	113	Alén	1 : 3 : 7	113	—	113	7
β	1 : ? : ?	90	Atterberg	1 : 3 : 8	87 and 90	—	89·5 and 85	2
δ	1 : 4 : 5	131	Atterberg	1 : 4 : 5	131	130	131	4
ε	2 : ? : ?	65	Cleve	1 : 4 : 6	66 and 56	66 and 56	66 and 56	6
ζ	2 : ? : β	56	Widman					
			—	2 : 3 : 5	109·5	—	109	2
			—	2 : 3 : 6	91	—	91	4

The value of this series of reference compounds in determining constitutions was demonstrated repeatedly in a series of some sixteen papers under the general heading " Studies on the Constitution of Tri-derivatives of Naphthalene ", published between 1890 and 1897. Special attention was paid to the naphthylaminodisulphonic acids, of which many were put at Armstrong's disposal by the German dyestuff firms, who obviously followed his work with the closest attention. One of the most valuable papers was undoubtedly that on the further sulphonation of the four isomeric heteronuclear β-naphthylaminemonosulphonic acids. In this paper was described for the first time (*Proc.*, 1890, 6, 129) 2 : 5 : 7-naphthylaminedisulphonic acid (from the 2 : 5-monosulphonic acid), which

by caustic fusion gives one of the most important intermediates for azo-dyes, 2 : 5 : 7-aminonaphtholsulphonic acid, the J acid of dyestuff chemists. This work also led Armstrong and Wynne to study the sulphonation of the chloronaphthalenemonosulphonic acids, and to compare the orienting influence of the chloro- and the amino-radical.

Among other naphthylaminedisulphonic acids of which the constitutions were determined by Armstrong and Wynne were the acids obtained by sulphonating naphthionic acid, known as Dahl acid II and III, which were shown to be 1 : 4 : 6- and 1 : 4 : 7-naphthylaminedisulphonic acid respectively; Schöllkopf acid, 1 : 4 : 8; ε-acid, obtained by the A.G.F.A. by nitration and reduction of Armstrong's 1 : 6-disulphonic acid, shown to be 1 : 3 : 8-naphthylaminedisulphonic acid; and a number of others.

Arising out of the work on ε-acid an incident occurred later which is worth recording, as it illustrates Armstrong's generosity in recognising the claims of others. Messrs. Kalle and Co. had obtained what was supposed to be 1-naphthylamine-3-sulphonic acid by removing one sulphonic group from ε-acid by reduction. Armstrong and Wynne confirmed this observation (*Proc.*, 1895, **11**, 238) and drew special attention to the fact that the 1 : 3-acid thus obtained corresponded with the description given by Cleve of an acid which he had obtained by reducing a nitronaphthalenesulphonic acid isolated from the nitration of naphthalene-β-sulphonic acid, and which he claimed had the 1 : 3-constitution. Neither Armstrong and Wynne nor other workers had been able to isolate the nitrosulphonic acid described by Cleve, but Armstrong and Wynne now provided decisive evidence that he had indeed obtained it.

All Armstrong's work on naphthalene was directed towards one end, the elucidation of the factors governing substitution in the naphthalene nucleus. He early recognised the so-called alpha law, that in substitution reactions the tendency is first for an α-hydrogen to be displaced, whereas β-substitution requires generally more drastic conditions. A second characteristic which he recognised was that, when a single substituent group is present in naphthalene which in benzene derivatives would give rise to *meta*-derivatives, a second substituent group enters the other nucleus, and a heteronuclear disubstituted naphthalene results. A phenomenon to which particular attention was paid was the isomeric change to which naphthalenesulphonic acids are prone, generally resulting in the conversion of an α- into a β-sulphonic acid. One such change was

discovered by Armstrong unawares. As early as 1881 (*Ber.*, 1882, 15, 200) he started a study of the sulphonation of β-naphthol, with the object of trying to cut down the large amount of sulphuric acid used by Schaeffer in preparing the acid known by his name. It was discovered that, sulphuric acid at a low temperature, or chlorosulphonic acid in carbon disulphide, being used, a sulphuric acid derivative of β-naphthol was obtained which could be readily hydrolysed back to β-naphthol, but which, by mere heating at water-bath temperature, was converted into Schaeffer's acid. He concluded that the readily hydrolysable derivative was β-naphthyl sulphate, $C_{10}H_7{\cdot}O{\cdot}SO_3H$, and it was not until 1893 that Tobias (G.P. 74,688) showed that it was in reality β-naphthol-1-sulphonic acid. Armstrong's mistake was excusable, for the instability of β-naphthol-1-sulphonic acid was unprecedented. The subject was taken up again in 1887, when the sulphonation of 1-bromo-β-naphthol was studied (this gave directly the bromo-derivative of Schaeffer's acid) and also the sulphonation of the " β-naphthyl sulphate ". The latter operation gave, not a "sulphosulphate", but " an isomeric disulphonic acid which is of special interest on account of the readiness with which, by mere warming with dilute sulphuric acid, it is converted into Schaeffer's β-naphtholmonosulphonic acid; there is little doubt that one of the sulphonic groups occupies an α-position contiguous to the OH " (*Proc.*, 1887, 3, 144). It is evident that Armstrong fully recognised the mobility of groups in the 1-position of β-naphthol, and was very close to forestalling Tobias's discovery made in 1893. Armstrong went on to study the sulphonation of β-ethoxynaphthalene with Amphlett, and of the β- and α-halogenonaphthalenes with Wynne, Sindall, and Williamson. The β-halogeno-compounds gave most interesting results. Sulphonated at a low temperature with chlorosulphonic acid in carbon disulphide, both the chloro- and the bromo-naphthalene gave as major product the 8-sulphonic acid with a little of the 6-sulphonic acid, but as the temperature of reaction was raised the proportion of the latter acid increased, and the 8-sulphonic acid could be converted into the 6-isomeride by heating at 150—160°. β-Iodonaphthalene, on the other hand, whilst giving, like the chloro- and bromo-compounds, the 8-sulphonic acid as major product, gave as a minor product not the 6- but the 5-sulphonic acid. It was argued from this circumstance that also in the case of β-chloro- and β-bromo-naphthalenes the 5-sulphonic acid is probably a primary product but is instantaneously isomerised to the 6-acid. This use of

the three halogens was a favourite resource of Armstrong's in attacking many problems in organic chemistry. He applied the method in studying the occurrence of iso-polymorphous series in benzenoid compounds and in his study of the strengths of aromatic sulphonic acids.

Later Armstrong and Wynne doubted whether the so-called isomerisation of naphthalenesulphonic acids is in fact such a phenomenon. More probably it is connected with the fact that α-sulphonic acids are more readily hydrolysed than β-sulphonic acids; in other words, α-sulphonation is reversible and β-sulphonation is not. Consequently, although the rate of β-sulphonation may be much slower than that of α-sulphonation, under appropriate conditions the former will be the final product. Alternatively a polysulphonic acid may be formed by β-sulphonation of the first-formed α-sulphonic acid, followed by removal of the α-sulphonic group. The former explanation was supported by the observation that in the chlorination and bromination of naphthalene a small proportion of the β-compound is formed along with the α-compound, proving a tendency, slow though distinct, to direct β-substitution.

In the course of his sulphonation studies Armstrong was impressed with the " invincible objection " of two sulphonic radicals to remain in contiguous or in *para-* or *peri-*positions to one another in the naphthalene nucleus when naphthalene or a substituted naphthalene is sulphonated. This behaviour made it impossible to obtain several of the theoretically possible di- and poly-sulphonic acids until, in 1892, a discovery was made in the laboratories of the Farbenfabriken vormals F. Bayer und Co. of a method for introducing a sulphonic group in place of an amino-group, the now well-known diazo-xanthate method. This process was revealed to Armstrong by Dr. Duisberg before the patent (G.P. 70,296) was published, and he and Wynne at once used it successfully for preparing the 1 : 2-, 1 : 4-, and 1 : 8-naphthalenedisulphonic acid (*Proc.*, 1893, 9, 166) from the corresponding naphthylaminesulphonic acids. The number of known disulphonic acids was thus brought up to nine of the ten theoretically possible.

In addition to all the work which has been described, much attention was paid to the chlorination and bromination of naphthalene and β-naphthol, and to the behaviour of the halogen derivatives with nitric acid and on sulphonation, the chief collaborators in this work being Rossiter and later W. A. Davis. These studies provided much evidence in favour of Armstrong's thesis that addition precedes substitution. The fact that bromination of naphthalene, unlike chlorination, gives no 1 : 3-di-derivative is explained by the fact

that naphthalene does not form a tetrabromide but does form a tetrachloride. Bromination of β-naphthol was shown to give the 1-bromo- and then the 1 : 6-dibromo-derivative, and Davis reduced the latter to 6-bromo-β-naphthol. Further bromination gave the 1 : 3 : 6-tri- and 1 : 3 : 4 : 6-tetrabromo-β-naphthols. Rossiter (*Proc.*, 1891, 7, 32) also claimed that sulphuryl chloride reacted with β-naphthol to give the 1 : 4-dichloro-derivative, but this interesting claim does not appear to have been confirmed. It was also observed that 1-bromo-β-naphthol formed an addition compound with nitric acid which decomposed in two ways, with acids to give β-naphthaquinone and with alkalis to give 1-nitro-β-naphthol. This observation gave strong support to the addition hypothesis to explain substitution.

In the course of the studies of isomerisation of naphthalene-sulphonic acids, Armstrong pointed out the tendency of naphthalene substitution products to assume a symmetrical structure. 2-Naphthol-6-sulphonic acid is an example of this tendency; similarly, α-chloronaphthalene, which at low temperatures gives the 4-sulphonic acid, at higher temperatures was found to give the more symmetrical 5-sulphonic acid, presumably by isomerisation. He also pointed out that symmetrically substituted naphthalene derivatives have higher melting points than those which are less symmetrical; thus of the dichloronaphthalenes the 2 : 6-compound has the highest melting point, the 2 : 3-isomeride having the next highest, then the 1 : 5-compound. This tendency for symmetrical to have a higher m. p. than unsymmetrical compounds is, however, subject to numerous exceptions, and it is evident that other factors come into play in determining fusibility.

Benzene.

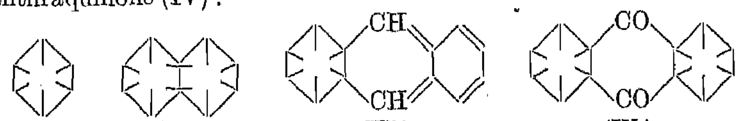
Armstrong was as interested in substitution in benzene derivatives as in naphthalene, and although he was born too late to be a pioneer in this field he nevertheless made important contributions to our understanding of the subject and in the course of his work developed clear-cut ideas. His work on the sulphonation of aniline and its derivatives is particularly important, as out of it arose the conception that the so-called *meta*-directing groups are those which have no *ortho-para*-directing influence, and are even inhibitors of *op*-substitution (*Proc.*, 1899, 15, 176). He showed that when amines are converted into salts they lose their *ortho-para*-effect; thus aniline in strong fuming sulphuric acid gave metanilic acid

(Armstrong and Berry, *Proc.*, 1900, **16**, 159). With Miss Evans it was shown that dimethylaniline gives the *p*-sulphonic acid with chlorosulphonic acid; in sulphuric acid it becomes more and more difficult to sulphonate as the quantity of acid present is increased, and to get the *m*-sulphonic acid strong fuming sulphuric acid is necessary. Another valuable line of work was the study of the bromination of ethers and esters of phenol and phenol-*p*-sulphonic acid, in which it was shown that some acyl groups, such as benzoyl, benzenesulphonyl, and benzylsulphonyl, completely protect the phenol-*p*-sulphonic acid from bromination. It was also shown that the benzeneazo-group can be displaced from benzeneazophenol by bromine exactly as the sulphonic group is from phenol-*p*-sulphonic acid.

Armstrong was the first to study systematically the recovery of hydrocarbons from their sulphonic acids by hydrolysis with aqueous sulphuric acid. This work was done in 1884 in collaboration with Miller (*J.*, 1884, **45**, 148), and it was shown that the sulphonic acids of different homologues of benzene, and naphthalene- and phenol-sulphonic acids require different strengths of acid and therefore different temperatures to effect their hydrolysis. It was attempted to use the method to effect separation of the hydrocarbons from mixtures by fractional hydrolysis of the sulphonic acids, but the temperatures of hydrolysis were not sufficiently sharply differentiated for this purpose.

The Kekulé formula for benzene did not satisfy Armstrong's desire to form a satisfactory mental picture of the benzene molecule and to represent it by a symbol free from ambiguity. His historic centric formula (I), which was suggested independently by Baeyer, was devised to meet the drawbacks to Kekulé's formula, that it represented benzene as having three ethenoid linkages, whereas it is in no way ethenoid, and that it implies the possibility of two different *o*-disubstituted derivatives.

In the centric formula the six central affinities were assumed to neutralise each other without constituting cross linkings within the ring. They were pictured as acting within a cycle rather than merely towards the centre. Armstrong later suggested the following "centric" formulæ for naphthalene (II), anthracene (III), and anthraquinone (IV):



(I.) (II.) (III.) (IV.)

Crystallography.

The work carried out on benzene derivatives in the laboratories at the Central Technical College was largely concerned with crystallographic studies. Amongst Armstrong's convictions when he started teaching chemistry at the Central was one that chemists would profit by a knowledge of crystallography, which had hitherto been the almost exclusive territory of the mineralogist. As all Armstrong's pupils knew, he constantly endeavoured to get them to think structurally in three dimensions. The idea that the crystal was the solid expression of molecular structure was always in his mind. In this, as in so many of his ideas, he was a pioneer. In 1886 H. A. (later Sir Henry) Miers, who was an assistant in the Mineral Department of the British Museum (Natural History), started a class in crystallography at the Central, at Armstrong's invitation, and among his pupils were (Sir) W. J. Pope, T. M. Lowry, and A. Lapworth. From that time until the closing down of the Chemistry Department in 1912, all the chemistry students had practical training in crystallography. The last instructor was T. M. Lowry, under whom the present writer studied the subject. This early introduction to a three-dimensional world undoubtedly determined the trend of the later interests of both Pope and Lowry.

It was usual for papers on chemical subjects from Armstrong's laboratories to include a detailed description of the crystals of the new substances reported. The laboratory was recognised as an institution at which new crystalline substances were welcomed as objects of investigation, and many research workers sent substances for crystallographic description. The results of work of this kind formed the subject of some fifteen "Mittheilungen aus dem krystallographischen Laboratorium des Central Technical College" in the *Zeitschrift für Krystallographie.*

For many years Armstrong was a member of a committee of the British Association the function of which was to study crystal morphology in the benzene series. The work carried out at the Central comprised the preparation and crystal measurement of isomeric mono- and di-halogen-substituted benzenesulphonyl chlorides and bromides, and resulted in the discovery amongst the chloro-, bromo-, and iodo-derivatives of several isopolymorphous series which were reported to the British Association. The development of the Barlow–Pope theory of crystal structure during the years 1906—08 gave the Professor great satisfaction, since it provided a working

hypothesis which he could apply to the data he had accumulated. The theory depended on two assumptions which have since proved to be untenable, that the volumes of the "spheres of influence" of the atoms in a crystal were proportional to their valencies, and that in the crystal the spheres of influence were close-packed. The writer and Dr. Colgate took up this study in 1910 and during four years examined the crystals of a very large number of derivatives of benezenesulphonic acid, checking and extending the work of earlier students. Several papers were published, and in the fifth of the series (*Proc. Roy. Soc.*, 1914, *A*, **90**, 111) the whole of the data was reviewed; their only value now consists in the crystallographic constants they record. The discovery of the *X*-ray method of investigating crystal structure by Laue, Friedrich, and Knipping in 1912 and its development by the Braggs and others provided a wonderfully precise weapon for studying the molecular architecture of crystals, and justified to the full Armstrong's belief in the importance of the subject, confirming his early confidence that crystal structure is determined by the arrangement of the atoms in the molecule.

The Origin of Colour.

Although Armstrong did not make any extensive experimental study of coloured compounds or dyes, he was the originator of an important generalisation which soon became one of the guiding principles of dyestuff chemists, the quinone theory of colour. One has only to read the short paper (*Proc.*, 1888, 4, 27) in which the theory is first put forward, to realise that it was not just a sudden flash of genius but the result of wide knowledge and deep thinking. Nor was Armstrong, as some critics have said, oblivious of the existence of colour on either side of the visible spectrum, for in the early part of the paper he says "the unsaturated hydrocarbons are not only more reactive than the paraffins, but the beginnings of colour are manifest in them if examination be made in the regions above and below the visible spectrum". After referring to the identity which had been discovered by Zincke and Bindewald of benzeneazo-α-naphthol and α-naphthaquinonephenylhydrazone he suggests that hydroxy- and amino-azo-dyes generally should be regarded as quinonic substances of the types

$$O\!:\!C_6H_4\!:\!N{\cdot}NHR \text{ and } NH\!:\!C_6H_4\!:\!N{\cdot}NHR$$

and he then goes on to propose quinone formulæ for such dyes as pararosaniline and methylene-blue. In a later paper he concluded

(*Proc.*, 1892, 8, 101) that the quinonoid origin of visible colour appeared to be so general that if a coloured compound was not quinonoid its formula was suspect. In this paper he suggested that *o*-nitrophenol must be quinonoid on account of its strong colour; he suspected that *m*-nitroaniline should be colourless if pure, but all his attempts with Kipping to remove its colour were fruitless, and he owned himself baffled. One of the most striking justifications of Armstrong's theory was the discovery of the deeply coloured quinones of polycyclic systems such as dibenzanthrene, many of which are valuable vat dyes. The writer cannot refrain from quoting the pregnant words used by Armstrong in the discussion of his second paper on colour, in reply to Ramsay: "It appeared probable that ultimately colour would be traced to that peculiar condition represented conventionally by a double bond, the atoms being regarded as altogether subordinate." This is very close to the modern view, fifty years later.

The Terpenes and Camphor.

One of the major preoccupations of organic chemists during the last quarter of the nineteenth century was the problem of the constitution of camphor and of the closely related terpenes. In this work Armstrong and his school, including Kipping, Pope, Lapworth, Lowry, and Forster, played a prominent part. Armstrong's first paper on camphor appeared in the *Chemical News* in 1878, when with Matthews he described a simple method for obtaining pure α-bromocamphor. A paper in the *Berichte* of the same year described experiments on the action of iodine on turpentine with production of cymene, and the following year appeared a long paper with W. A. Tilden (*J.*, 1879, 35, 733) describing experiments on the action of sulphuric acid of different concentrations and at different temperatures on American and French turpentine, and demonstrating the complex nature of the changes which take place. The steam-volatile, optically inactive product of the action of concentrated sulphuric acid on turpentine, which had been given the name "terebene" by Deville in 1840 and was apparently regarded as a chemical individual, was shown to consist largely of camphene, together with some cymene and a hydrocarbon $C_{10}H_{20}$. A more dilute acid produced principally "terpilene" (terpinolene, Wallach), the structure of which was later established by Baeyer.

The so-called "colophene" (the non-volatile product of the action

of sulphuric acid on turpentine) was shown to be probably a mixture of polymers. Armstrong and Tilden also studied the oxidation of camphene and of camphor. From *dl*-camphene, by oxidation with dichromate and sulphuric acid, they obtained *dl*-camphor; this, by further oxidation with nitric acid, was converted into *dl*-camphoric acid, which had been previously made by Chautard by mixing the optically active forms.

In 1883 Armstrong and Miller studied the action on camphor of zinc chloride, iodine, phosphoric oxide, and phosphorus pentasulphide. The reactions are highly complex: from the product of the dehydration of camphor with zinc chloride, for example, there were isolated *p*-cymene, 1 : 2-dimethyl-4-ethylbenzene, 1 : 2 : 3 : 5-tetramethylbenzene, and carvacrol.

In 1891 Armstrong investigated the crystalline alcohol, $C_{10}H_{18}O_2$, produced from oil of turpentine by atmospheric oxidation in presence of sunlight, and gave to it its present name, sobrerol (after Sobrero, who first isolated it in 1851). He isolated the dextrorotatory form of sobrerol from American oil of turpentine and also from a Burmese oil, and the lævorotatory form from French oil. With Pope, he published a crystallographic study of the hemihedral crystals of the two enantiomorphs, and also of the racemic compound prepared by mixing them and crystallising.

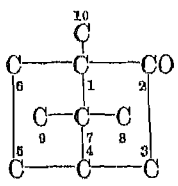
In 1893, continuing the experiments which had been begun earlier with Miller, Armstrong in collaboration with Kipping, studied the product of reaction of camphor with hot concentrated sulphuric acid. By this process, Delalande, in 1839, had obtained an oily product to which Chautard in 1856 had given the name "camphren". Camphren was later investigated by Schwanert and by Kachler, with varying results. Armstrong and Kipping showed that crude camphren contained, in addition to unchanged camphor, 1-acetyl-3:4-dimethylbenzene (isolated by its phenylhydrazone) and a substance of peppermint-like odour which yielded α-methylglutaric acid on oxidation. The complete structure of this substance, now known as carvenone, was determined later by Tiemann and Semmler.

To Armstrong's school belongs the credit of first preparing a sulphonic acid of camphor, although the action of sulphuric acid on camphor had previously been studied by many other workers. The work was carried out by Kipping and Pope from 1893 onwards, but the hand is obviously the hand of Armstrong. All the features of the naphthalene research are present, the careful investigation of conditions using fuming sulphuric acid and chlorosulphonic acid,

the isolation and purification of sulphonyl chloride and sulphonyl bromide, finally the pyrogenetic decomposition of these with formation of new chloro- and bromo-camphors, the π series, as they were named and are still called. Corresponding π-sulphonic acids were obtained from α-chloro- and α-bromo-camphors, and these acids of the π series were later used by Pope and by others for the isolation of optically active compounds containing asymmetric atoms of nitrogen, sulphur, silicon, tin, and other elements.

With Lowry, Armstrong carried out important work on the constitution of the sulphonic acid of camphor first prepared by Reychler in 1898 by the action of a mixture of acetic anhydride and sulphuric acid on camphor at the ordinary temperature. Reychler converted his acid into the corresponding amide, of which he obtained two forms; he considered the acid to be the α-sulphonic acid and the two amides to be stereoisomeric forms. Armstrong and Lowry applied Reychler's method to α-chloro- and α-bromo-camphor and obtained corresponding sulphonic acids from them, and found that by dehalogenation by reduction the amides gave one or other of Reychler's camphorsulphonamides. Eventually it was found that Reychler's two "sulphonamides" were not isomeric, but that one was an anhydride formed by loss of water from the other. Further consideration of the properties of the sulphonic acids, and especially the impossibility of oxidising them to camphoric acid, led to the conclusion that the sulphonic group could not occupy the α-position, and this conclusion was confirmed by the discovery that thermal decomposition of the sulphobromide gave a new (β-)bromocamphor, which was also prepared at about the same time by Forster by another method. Reychler's acid must therefore be the β-sulphonic acid.

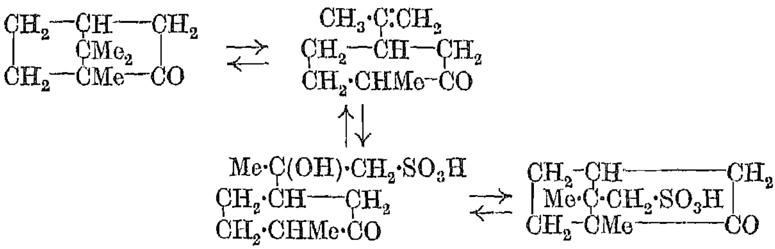
The identity of the β-position in the camphor skeleton was unknown. On the evidence available, two positions were possible, carbon atoms 6 and 10 in the inset diagram. Both Armstrong and Lowry and also Forster favoured carbon 6, and it was not until 1923 that Wedekind, Schenk, and Stüsser (*Ber.*, 56, 633) obtained evidence showing that carbon 10 is almost certainly the β-carbon. The anhydride formation from the sulphonamide, in which the keto-group is involved, indeed seems much more understandable if the sulphonic group is on carbon 10. Later Lipp and Lausberg



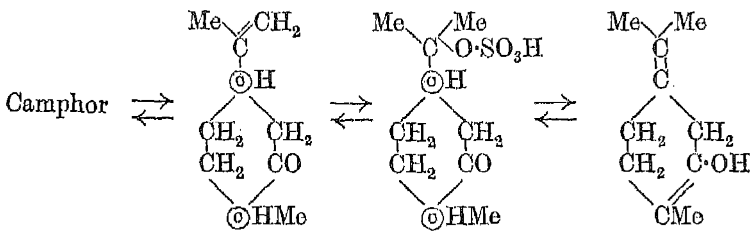
(*Annalen*, 1924, 436, 274) concluded that β-bromocamphor is the

10-bromo-compound, confirming Armstrong's and Lowry's view that no change of orientation occurred when the sulphobromide decomposed into β-bromocamphor.

In their third paper on camphor Armstrong and Lowry (*J.*, 1902, **81**, 1469) discussed the mechanism of the complex changes associated with substitution in and " dehydration " of camphor. The view is held that changes are initiated by addition at the keto-group. The process of π (*i.e.*, 8)-sulphonation, discovered in Armstrong's laboratory by Kipping and Pope, is supposed to involve the rupture of the bond between carbons 1 and 7 at an early stage and may be represented schematically thus :



This mechanism is supported by the known formation of carvenone by the action of sulphuric acid on camphor; and by the formation with the same reagent of acetyl-*o*-xylene observed by Armstrong and Kipping. It also fits in with the racemisation of camphor when converted into the π-sulphonic acid observed by Kipping and Pope, but to account for this phenomenon completely, inversion of the other optically active carbon atom, No. 4, must occur. Enolisation must be involved, and the complete scheme to account for racemisation is :



The well-known work of Lapworth and Forster on camphor chemistry was initiated in Armstrong's laboratory. Finally mention must be made of Lowry's important work on nitrocamphor leading

to the discovery of the phenomenon of mutarotation, which was traced to the change

$$C_8H_{14}\Big\langle\begin{matrix}CH\cdot NO_2\\ |\\ CO\end{matrix} \longrightarrow C_8H_{14}\Big\langle\begin{matrix}C:NO\cdot OH\\ |\\ CO\end{matrix}$$

The same phenomenon was observed with π-bromonitrocamphor and the now well-known term "dynamic isomerism" was coined to describe the condition of such substances. Armstrong's work in the camphor field was thus not only valuable in itself but an inspiration to others.

The Theory of Aqueous Solutions.

Armstrong's independence of thought showed up most strongly in his determined and prolonged opposition to the ionic dissociation hypothesis as developed by Arrhenius, van 't Hoff and Ostwald ("the Three Musketeers of Physical Chemistry" as he styled them) to explain the electrical conductivity of aqueous solutions of salts, acids, and bases. His attitude was indeed consistent with his whole chemical philosophy. He had pondered deeply on the processes of chemical change, and had come to the conclusion that such changes were preceded by association of the interacting substances. The idea of the spontaneous dissociation of a molecule into charged ions was therefore distasteful and contrary to his chemical feeling. Equally important in determining his attitude was his conception of water. "Water", he says, "is of all substances known to us not only the most active and useful but the most marvellous." How then should this powerful substance behave merely as a medium for the dance of the ions, or as a screen to keep them apart? The supporters of the theory of ionic dissociation concentrated their attention on what happened to the solute and ignored the solvent. Armstrong insisted that the solvent and the solute must play reciprocal parts in any conducting solution. He also pointed out that the mathematical formulæ on which the "ionists" relied held true only for very dilute solutions of those substances which in water formed electrolytes; that is to say, they only held true when water was in great excess. The properties of such solutions were therefore surely due to the effect of the dissolved substance on the water!

In 1909 Armstrong produced two lyrical essays on water, the very titles of which are characteristic of the man: "A Dream of Fair Hydrone" and "The Thirst of Salted Water". In these two

papers we get the whole case against the ionic theory, supported by apt allusion and quotation, gentle ridicule and serious warning against mass suggestion. Armstrong was one of those rare men whose heterodox opinions have a way of coming true at a later date, perhaps not exactly as he expressed them, but very nearly so. In the papers just quoted he discusses and compares the hydrides of carbon, nitrogen, oxygen, and chlorine, showing that, from its physical properties alone, water must be a complex substance, not aitch-two-oh! He then goes on to compare the behaviour of hydrogen chloride towards ammonia and unimolecular water, which he proposes to call " hydrone ". He supposes that, just as ammonia combines with hydrogen chloride to form ammonium chloride, nitrogen passing from the tervalent to the quinquevalent stage, so hydrone combines with hydrogen chloride to form the complex $H_2O{<}^{Cl}_{H}$, in which the oxygen becomes quadrivalent. One must admit that this is a remarkable prevision of modern views based on the octet theory, although Armstrong could not foresee that the above complex should be divisible into the ions OH_3^+ and Cl^-, as ammonia gives NH_4^+ and Cl^-. He considered that radical exchange was reciprocal in a solution of hydrogen chloride in water, with formation of two kinds of complex, $H_2O{<}^{H}_{Cl}$ and $HCl{<}^{H}_{OH}$, and that electrolysis involved interaction of both. He was careful to point out that he did not conceive that simple hydrate formation would account for the production of electrolytes, but that some reciprocal effect between solute and solvent was to be looked for.

That a salt or acid dissolved in water was in any way comparable with a gas was a view strenuously opposed by Armstrong, whatever mathematical analogy might be discovered by van 't Hoff and others. Fitzgerald had advanced cogent arguments against the conception in his Helmholtz Memorial Lecture to the Chemical Society in 1896, and Armstrong took his stand largely on Fitzgerald's views. He found an explanation for osmotic effects in the complex nature of water and the effect thereon of dissolved substances. Thus osmotic pressure became, in his view, " the Thirst of Salted Water ". Water is a complex $(H_2O)_x$ saturated with the " gas " hydrone, H_2O. A solute combines with the hydrone, thereby lowering the vapour pressure. The osmotic pressure manifested by such a solution is the hydraulic pressure exercised by the extra molecules of hydrone attracted into it by the distributed complexes. These ideas

are elaborated in several papers, especially "The Origin of Osmotic Effects" (see "The Art and Principles of Chemistry", Ernest Benn, Ltd., 1927).

Experimentally Armstrong attacked the problem of aqueous solution from a number of directions. Particularly he studied the displacement of salts from solution by inorganic and organic solutes; the rate of hydrolysis of esters by acids of all kinds, and the effect of the presence of salts; and the hydrolysis of sucrose and other carbohydrates by acids and by enzymes. During the years 1906—13 papers of the series "Processes Operative in Solution", over thirty in all, appeared at regular intervals, most of them in the *Proceedings* of the Royal Society. The collaborators were Caldwell, Whymper, Watson, Glover, Eyre, Wheeler, Crothers, Walker, Worley, and others. It would be impossible here to attempt to summarise all this work. The experiments on the hydrolytic activity of acids, however, must be mentioned. These drew attention to a fact which was already known to Ostwald, that the activity of acids increased with increasing concentration, whereas if, as the supporters of ionic dissociation maintained, hydrogen ions were the active agents, hydrolytic activity should increase with increasing dilution. Another difficulty for the dissociationists was that the hydrolytic activity of acids was increased in the presence of their salts. Armstrong therefore concluded that hydrolysis had nothing to do with hydrogen ions but was effected by the break-down of a system composed of the hydrolyte, the catalyst, and water. The process was therefore parallel to that of hydrolysis by enzymes, apart from the fact that the latter are specific in their action whilst acids are not.

The controversies have died down. Most chemists leave consideration of such matters to the specialists, the physical chemists, and believe what they are told. Nevertheless, the perplexing problems presented by aqueous solutions, so clearly perceived by Armstrong, are still problems. New knowledge has brought modifications to the ionic dissociation theory, and some of Armstrong's criticisms have been justified.

Parallel with his studies on processes operative in solution, Armstrong was producing two other series of papers, one on the "Origin of Osmotic Effects", the other on "Enzyme Studies". Under Armstrong's treatment these investigations were closely related to his studies of solutions. In the former series he brought into his orbit differential septa such as the covering of the seed of the barley, *Hordenum vulgare*, on which some curious observations

had been made by Adrian Brown (1909); and the substances which stimulate enzyme activity by penetrating the leaves of plants (1910). The enzyme studies were carried out in collaboration with his son E. F. Armstrong, Glover, Eyre, Horton, and a number of occasional helpers. Dr. J. V. Eyre in 1916 contributed an admirable summary of the work to the *Central* (Vol. 13, No. 39, Aug., 1916). The work was started in 1900 with the object of studying quantitatively the hydrolytic action of enzymes, especially on biose sugars. It was shown that, in absence of other disturbances, the rate of hydrolysis was constant and dependent only on the amount of enzyme present. From this and other data gained from a study of the influence of the products of change, it was concluded that hydrolysis occurred at the surface of the colloid particles of the enzyme, to which were attracted active molecules of water and molecules of the sugar. The early experimental work was done on lactase, maltase, invertase, and emulsin. Later an important study was carried out on urease, the urea-splitting enzyme, when it became known from the work of Takeuchi that this enzyme was readily obtainable from soya bean. Only the briefest mention can be made of the intensely interesting work on the cyanophoric glucosides and corresponding enzymes occurring in the bean *Phaseolus lunatus*, in cherry laurel (*Prunus laurocerasus*), in different species of flax, and in such herbage plants as birdsfoot trefoil (*Lotus corniculatus*) and white clover (*Trifolium repens*). In the cherry laurel a new enzyme was discovered which, whilst without action on amygdalin, hydrolysed prunasin, the glucoside left after one half of the glucose of amygdalin has been removed. The new enzyme, prunase, must therefore be present in the complex enzyme emulsin. Subsequently the glucosides linamarin, amygdalin, prunasin, and salicin were used as test substances in seeking for enzymes in the leaves and seeds of a very large number of plants. It was found that the occurrence of cyanophoric glucoside in white clover and birdsfoot trefoil was fortuitous and inexplicable, and the opinion was expressed that variations in enzyme and glucoside content might have an important bearing on the value of such plants as feeding stuffs. Unfortunately this important and original line of work was cut short at the flood through the dispersal of Armstrong's collaborators when his chemistry school was closed down.

Reference was made on p. 84 to Armstrong's conceptions of the mechanism of chemical change. These views were based on those of his spiritual master, Faraday, whose work on electrolysis

he regarded as one of the masterpieces of all time. Every one of his students was urged to read and study Faraday's electrochemical researches. "All ordinary chemical actions are themselves electrical." To understand any chemical reaction, look for the electrolyte. Two pure substances cannot interact. Chemical reaction is a kind of reversed electrolysis, requiring for its progress a complete electric circuit. These ideas were forming in his mind as early as 1880, being strengthened by H. B. Dixon's observation in that year that water vapour was necessary for the combustion of carbonic oxide in oxygen. The striking results obtained by H. B. Baker on the effects of intensive drying in slowing down and even preventing combustion lent confirmation to his views, and in 1885, discussing one of Baker's papers at a Chemical Society meeting, he said that "he had ventured to affirm to Mr. Dixon that some day it would be ascertained that a mixture of pure oxygen with pure hydrogen was not explosive". Seventeen years later Baker himself showed that it was possible to prepare an intensively dried mixture of oxygen and hydrogen which did not explode when sparked, and Armstrong's prediction was fulfilled. It also appeared from Baker's experiments that water alone did not suffice to make such a mixture explosive, but that something more was needed. In Armstrong's view the missing substance was something to render the water a conductor and complete the electric circuit. In spite of all evidence to the contrary he maintained that water—pure water—must be a perfect non-conductor. If the purest water obtainable still had a measure of conductivity, it was not pure water. On this question, as on some others, Armstrong allowed his feelings to go beyond the evidence.

The rusting of iron was another subject in which Armstrong took a lively interest, both because of the technical importance of the subject and because rusting was a process suspected from early days of having a voltaic origin. He believed that atmospheric corrosion would be impossible, even in presence of air and water, unless an electrolyte were present. G. T. Moody was able to show experimentally at the Central that iron could be kept indefinitely uncorroded in presence of water and a current of air from which carbon dioxide was rigidly excluded; as soon as air containing carbon dioxide was admitted, rusting commenced (*J.*, 1906, **89**, 726). Armstrong's view was that the first product when iron rusted in air was a soluble ferrous bicarbonate which was oxidised by air to an insoluble ferric compound, and in support of this Moody devised a

very simple experiment. Some bright nails were put in a glass cylinder and covered to a depth of about an inch with water; a disc of filter-paper was put in the water over the nails. In time a stain of rust appeared on top of the filter-paper, the nails being practically untarnished, showing that the rust was deposited from the water. Moody's experimental results on the influence of carbon dioxide on rusting were challenged on the ground that his iron had been rendered passive before the experiment by treatment with chromic acid, and a good deal of controversy arose. Whether the simple question which these experiments tried to answer has yet been definitely settled the writer would not dare to assert.

Armstrong's beliefs regarding the mechanism of chemical change were given fully in his Presidential Address to the Chemical Society (*J.*, 1895, 67, 1122); they subsequently underwent little modification, and pervade most of his chemical writings.

Any notice of Armstrong's life and work would be unbalanced without considerable reference to his labours in the field of education, for his name must be prominent in the history of educational reform during the last two decades of the nineteenth and the opening years of the twentieth century. The deficiencies in our educational system became apparent to him in his early teaching days at Finsbury, and he soon made up his mind that the poor quality of the average boy coming to be taught chemistry and physics was largely the result of bad elementary education. The prospect of starting a campaign against the notoriously conservative British forces of education would have daunted most men; but not Armstrong, in spite of his preoccupation with higher technical education and chemical research. He was, in fact, firmly convinced that higher education in technical subjects could only be properly built up on a satisfactory basis of elementary education.

Armstrong's first public pronouncement on methods of teaching science was made in a paper read before an International Conference on Education in 1884. In this paper he first advocates the teaching of the general science of daily life by setting the pupils to carry out practical experiments so designed that the students find out things for themselves. At the same conference a paper on somewhat similar lines was read by Professor Meiklejohn, who used the term "heuristic" to describe this style of teaching. The dictionary definition of the word is "serving to discover"; it was not to be found in a dictionary at that time. Armstrong was in rebellion

against the practice of teaching scientific subjects by the didactic methods, almost universal at the time, acquired from the teachers of classical and humanistic subjects. Science is an ever-growing body of knowledge acquired by experiment, observation, and use of the imagination, not a static collection of dogmas. In his view the only satisfactory way to teach it is by leading the young student by suitable paths to experiment and discover for himself, making every use of the natural inborn curiosity which he believed every child to possess. He adapted a saying of Lessing to emphasise the difference between didactic and heuristic methods: "If the Almighty were in the one hand to offer me Truth and in the other the Search after Truth, I would humbly but firmly choose the Search after Truth." Many years of hard work followed before Armstrong saw the truth of his arguments becoming acknowledged and the methods he advocated adopted. He worked largely through the British Association, which in 1887 formed a committee "for the purpose of enquiring into and reporting on the present methods of teaching chemistry in schools"; its members were Armstrong, J. T. Dunn, W. R. Dunstan, J. H. Gladstone, A. G. Vernon Harcourt, Francis Jones, R. Meldola, Pattison Muir, W. J. Russell, W. A. Shenstone, Professor Smithells, and Mr. Stallard—a truly representative body. Equally impressive are the names of the committee on "The Teaching of Science in Elementary Schools" which was working at the same time: Armstrong, Lydia Becker, Sir John Lubbock, Sir Richard Temple, Sir H. E. Roscoe, James Heywood, N. Story Maskelyne. The first committee issued two important reports in 1889 and 1890, in which were included lengthy suggestions for elementary experimental courses in chemistry, entirely the work of Armstrong. These recommendations were, in part at least, taken into consideration by many educational and examining bodies, and played a very large part in reforming the teaching of science. Armstrong's many essays and addresses on the subject, including the British Association report, are included in his book "The Teaching of Scientific Method", 3rd Edition, 1925.

He was helped by a number of devoted disciples, notably by Hugh Gordon, an Oxford graduate who worked amongst the teachers of the Surrey Council Schools and later for the London School Board; by E. M. Rich, who worked in Staffordshire and Ireland and later became Director of Education under the London County Council; and by W. M. Heller, who carried reform into the National Schools of Ireland against much opposition. Mr. C. E. Browne successfully

introduced Armstrong's methods in the very letter and spirit, at Christ's Hospital. Armstrong's own first-year chemistry course at the Central Technical College was essentially heuristic in character. The engineers, who formed the majority of his students, made some fun of it; but many expressed appreciation of the value of the training in after life. The method is slow at first but it does inculcate sound principles and habits. To the last Armstrong was dissatisfied with the results of his efforts in the educational field. That his fears were not groundless and that the unimaginative, conservative spirit which he fought so strenuously to reform still lingers unregenerate in dark places is shown by a letter in *Nature* of July 27th, 1940, from a schoolmaster who, discussing practical science teaching in public schools, proposes abolishing all practical work until after the school certificate examination, and cramming every boy, regardless of his capacity, with Latin. "Two good science lectures weekly, with demonstrations", he maintains, "are all that are required". It is because of this spirit in educational circles that the level of appreciation of the potentialities of science is so low amongst our general public, our business men, and our administrators. In spite of such die-hards there is no doubt that revolutionary changes have taken place since Armstrong began his campaign over fifty years ago, and these changes are due more to him than to any other man. It must be recorded that it was he who induced the Council of the British Association to establish the Educational Science Section in 1901, against much opposition. He devoted much time to putting it on its feet in its early days, receiving enthusiastic support from Sir Philip Magnus.

As a teacher himself Armstrong was incomparable. He lectured, at South Kensington, only to the first-year students, since he regarded the ground-work as of the greatest importance. Although his methods were essentially heuristic, leading the student on from one discovery to another, he yet covered an amazing amount of ground, and any student who followed his course carefully had a sound knowledge of the fundamentals of theoretical and inorganic chemistry, and also an appreciation of the history and growth of the science. The lectures were abundantly illustrated with carefully designed experiments which seldom failed.

His instruction of the senior chemistry students took the form of discussions rather than formal lectures. Listening to him we felt and knew that everything he told us was the outcome of his own experience and deep thinking, that we were not merely being told

uncritically what other people thought. If we did not profit from his teaching, our own stupidity was to blame.

Text books were abjured ("in our subject they are rarely otherwise than collocations of dogmatism and narrow mindedness") but for general reading he recommended Kingsley's "Town Geology", Cooke's "New Chemistry", Black's "Magnesia Alba", and Faraday's "Researches in Electricity", all calculated to imbue the student with the spirit of science.

Armstrong found time, amongst all his other activities, to be an active Governor of two important schools, first St. Dunstan's College, Catford, and then Christ's Hospital, he being appointed to represent the Royal Society on the Council of Almoners of the latter school in 1896. To Christ's Hospital he gave invaluable, unstinting service. The removal of the School from Newgate St. to West Horsham in 1902 gave the opportunity for building new modern laboratories for science teaching. The design and equipment for these were his special care, besides such matters as water supply, drainage, and sewage, and he paid close attention to the diet of the boys. Workshops for manual training were built and equipped at his instigation, and a revolution took place in the provision for art training. Owing to his efforts the school, which had been traditionally devoted to classics and mathematics, became the best-equipped school in the country for science teaching. As late as 1929 he supervised the building of a new science block made necessary by the expansion of the needs of the school. It was at Christ's Hospital that he found the best opportunity for putting into practice heuristic teaching at a school, for at first the institution was free from interference from outside examining bodies. In 1908, however, the school was obliged by the Board of Education to adopt the School Certificate Examination as a criterion of efficiency, and the heuristic teaching had to be modified to meet the requirements of the examination syllabus. The spirit of the method was, however, maintained. Armstrong was deputy chairman of the school's Education Committee from 1916 to 1930, then Chairman up to 1937, when he retired owing to ill-health and was appointed Education Adviser by the Council as a mark of their appreciation of his great services.

Armstrong's many and diverse activities outside the fields of chemical research and teaching would require a full-scale biography for adequate description and appreciation. Here they can be no more than touched upon. His intense interest in agriculture found

expression in his long connection with Rothamsted, where he represented the Chemical Society on the Lawes Agricultural Trust Committee from its inception in 1889, becoming vice-chairman in 1918 and chairman in 1937, shortly before his death. He was responsible for inducing the Indian Government to start a Research Institute for studying indigo cultivation in India in 1915, believing firmly that under scientific control the natural product could compete with the synthetic, with immense benefit to Indian agriculture. Unfortunately the experiment, which was producing results, collapsed under the economy axe in 1923. His experiences in India and elsewhere made him an enthusiastic advocate of the methods preached by Sir Albert Howard for utilising vegetable and animal refuse for enriching the soil. Pasteurisation of milk was a subject on which he held strong views, believing the practice to be wrong in principle; the tuberculous cattle should be eliminated. His friends will all remember his strong support of the British dyestuff industry and his very personal method of showing his enthusiasm by appearing at evening functions, at home and abroad, in a brightly dyed waistcoat. The waistcoat of Caledon Jade Green was perhaps the most becoming of his collection, although the one of indigo-blue with thioindigo-red facings was the most striking. At the Faraday centenary exhibition at the Albert Hall in 1931 he organised, on chemical lines, a wonderful exhibition of dyed fabrics and pigments. This exhibition was subsequently shown at a Friday evening lecture at the Royal Institution.

He had his vision of a Utopia in which the science of chemistry came into its own. He gave expression to his shape of things to come in an address " As it should be to-morrow " to the Frankland Lancastrian Society, June 18th, 1935. Since by eating we live, there should be intensive research on the influence of food on growth, both of plants and animals; particularly the influence of soil factors and fertilisers on the growth of plants must be studied. Correct feeding he believed to be the true basis of health, and the chemist must discover what correct feeding is. At the end of seventy years of study he says, " Chemistry is, after all, the science of life—as such, very difficult." In national affairs he saw the need of controlling man's actions against his most deeply ingrained instinct—the sin of covetousness, the mainspring of all commerce. Against the uncontrolled waste of industrialism, especially in our use of coal, he cried out again and again in speeches and in letters to the Press. Above all he wanted to see organised planning by

enlightened leaders, and deplored ignorance in high places of the findings of science and the importance of these discoveries in the lives of the people. He desired to see scientific men take their place as leaders in public affairs.

Of his work for the Chemical Society mention has already been made. His address in 1894 on the affairs of the Society is worth reading again for the picture he gives of what were and should be the scope of the chemist's activities. Much of what he foresaw has come true. Even at that time he advocated joint publications with other societies, a course to which we are now being driven. He warned the Universities and chemical manufacturers of the dangers of neglecting chemistry, fearing that our awakening would come too late and that America would go ahead of us as a chemical manufacturing country. This last prophecy is being fulfilled before our eyes. He recommended the examination and exploitation of the natural products of India and the Colonies, a matter in which we still lag behind. The whole address is still apposite; Armstrong's writings, like Shakespeare's, do not get out of date, because he dealt with fundamentals, not with superficialities.

Having lived through such stirring times in the growth of science, and known so many of the leading scientists of his time, Armstrong was specially fitted in later years to recall to the younger generation the history of his beloved science. This he did in many addresses, memorial lectures, biographies, and lighter essays. This phase of his activity was foreshadowed in his Hofmann Memorial Lecture (*J.*, 1896, **69**, 637), which is a masterly summary and appreciation of the work of the great German chemist. Armstrong's writings on the famous chemists of his time are not only first-rate history from the pen of a contemporary; they are vivid and exciting in style, penetrating in their analysis of character and achievement, whilst reflecting throughout the qualities and ideals of the writer. Collected and reprinted as a volume, they would form a valuable addition to the history of chemistry.

Armstrong was the recipient of many honours. These included the LL.D. of St. Andrews; the D.Sc. of Melbourne and Madrid; the Davy medal of the Royal Society, the Albert medal of the Royal Society of Arts; the Messel medal of the Society of Chemical Industry and the Horace Brown medal of the Institute of Brewing.

To those who were privileged to know him intimately Armstrong was a man of great charm and a warm personal friend. He never forgot or neglected responsive students; he placed them in suitable

posts and was always ready to help them on their way through life. Generally they well repaid his trouble. Many rose to high positions in industry, others in the academic world. He had much artistic taste, especially for pictures and pottery. He loved music, especially the opera, and although he admired Wagner and heard the "Ring" whenever possible, he could appreciate the simpler melody of Mozart. He cultivated his garden and was fascinated by the colours of flowers. For holidays he chose the Lake district, being faithful to his early love of Borrowdale. Here he had parties in spring and autumn, generally inviting one or two of his senior students or staff to join him and his family. The simple pleasure of leading an expedition up Sca Fell Pike or Great Gable gave him the greatest satisfaction. Mrs. Armstrong shared her husband's interest in his students and rivalled him in her wonderful memory, even in extreme old age, of everything concerning them.

Armstrong married on August 30th, 1877, Frances Louisa Lavers, and had seven children, four boys and three girls. He and his wife celebrated their golden wedding in 1927, and Mrs. Armstrong died shortly before her husband, in her ninety-third year. Her fidelity and sympathy to her busy, and probably sometimes difficult, husband during that long period were gifts which he frequently acknowledged with deep gratitude.

A brilliant portrait of Armstrong was painted in 1927 by T. C. Dugdale, R.A., and was exhibited at the Royal Academy. It was purchased by Armstrong's past students and staff and was presented to Professor and Mrs. Armstrong on the occasion of their golden wedding. It shows the Professor in a characteristic attitude holding one of the atomic models with which he was speculating at the time. After his death it went to the Royal Institution, a worthy place, but one feels it would be more at home in the rooms of the Chemical Society. For Armstrong was, first and last, a chemist. "Chemistry", he wrote, "is an art as much as a science, and the chemist is full of feeling which cannot be quantified". He himself was full of this feeling of which he wrote, and his great services to chemistry cannot be weighed and measured. His mission in life was to serve the advancement of the science of chemistry and its application to social well-being in the widest sense. He carried on his mission to the end with the fervour of a prophet, and his name will not be forgotten.

RAPHAEL MELDOLA

1849—1915

RAPHAEL MELDOLA came of an ancient Spanish stock—the Sephardic family, who trace their ancestry back to the thirteenth century—some of whom migrated from Toledo to Ravenna and later to England. He was born at Islington, London, on July 19th, 1849, the son of Samuel and grandson of Raphael Meldola, then Chief Rabbi of London. The name Meldola is believed to have been adopted many years ago by a branch of the family who lived at the small town of that name not far from Ravenna: this ancient custom of taking a place name to assist family identification survives in Wales to this day.

After attending private schools at the village of Kew and later on the very fringe of London, at Maida Vale, Raphael Meldola entered the Royal College of Chemistry in Oxford Street, London, in 1866, at the age of seventeen. He was a small, spare young man, never robust, and probably for that reason as well as from choice he took no part in the rough and tumble of games, preferring to spend his leisure in roaming the countryside in search of natural objects of interest. He is said to have been modest and shy, whilst showing in conversation and address a youthful dignity and thoughtfulness which developed into the clarity and precision in speech and writing for which he became distinguished in later life. Meldola was endowed with an active, enquiring mind and quite early his gift of quick and precise observation and love of detail found free play in the study of natural history. His early friendship, too, with John Keast Lord, the naturalist, while at the College of Chemistry, did much to develop that strong inclination towards natural history which he retained throughout his life. Professor E. B. Poulton, in his admirable obituary notice of Meldola, refers to this friendship, and how he found the following written in Meldola's copy of Lord's book "At Home in the Wilderness" (1867): "This book was written by my first natural history friend—my ideal of manliness—my first subject of hero worship as a youth. His death in 1872 was the first real grief

RAPHAEL MELDOLA

I ever experienced. I was with him at Brighton almost to the end. Raphael Meldola."

During those years at college Meldola met as a fellow student (Sir) Alexander Pedler, the astronomer, with whom he formed a strong and lasting friendship. Henry E. Armstrong had entered the College in the previous year, and there were at the time several other young men who, like himself, were destined to play an important rôle in the future development of science in this country. Whereas some, like Armstrong, came without any marked inclination towards one or other of the branches of natural science provided at the college, Meldola came to study chemistry and allied subjects with a strong predilection for entomology and nature study. There is no doubt that Meldola was before all things a naturalist. Whatever other branches of science and learning occupied him, his interest in them became the more keenly aroused when they could be brought to bear upon his favourite subject.

The course at the Royal College of Chemistry under Dr. Edward Frankland undoubtedly provided a broad and liberal scientific training, and after two years, at the age of nineteen, Meldola received the certificate of the College for proficiency in chemistry. He then, in 1868, became assistant to Dr. John Stenhouse, Assayer to the Royal Mint, with whom he remained until 1871, when the post of Assayer was abolished. One cannot help feeling that this appointment must have been greatly to his liking, for it involved the exercise of a high degree of accuracy in analysis, which accorded with his temperament, and the demand upon his time could not have been serious because during those three years he was able to follow his natural history work with great attention and success. His first publication in the *Entomologist* appeared in 1869, followed during 1870—71 by a series of articles on "Caterpillars and their Foes" and other contributions on natural history which were published in *Land and Water*.

His friends and contemporaries of those days speak of Meldola as a first-class field naturalist, with highly developed powers of observation and perspicacity, a lover of great detail and meticulously accurate in all departments of his work. With this background he became in later years a broad thinker and a clear writer, unafraid of the limitations of the systematist and refreshing in the way he brought knowledge and experience of one subject to bear upon another. Moreover, he was blessed with a marked power of concentration and a highly retentive memory. Thus, early in life,

Meldola must have been a man of singularly attractive personality with a rich capacity for forming friendships. Yet amid all these circumstances of temperament, predeliction, and opportunity, he entered the realm of industrial chemistry in 1871 by joining the Staff of Williams, Thomas and Down, colour manufacturers at the Star Chemical Works, Brentford. There is little doubt, however, had he been free to choose, he would have made his career as a naturalist.

At that time industrial chemistry was scarcely a profession in this country, although in Germany it was offering great opportunities: it needed the passage of many years before the application of science to industry was even remotely comprehended in England. From brief references and remarks it seems clear this occupation at Brentford offered very little scope and was not attractive, but it undoubtedly aroused in him an interest in colour and its origin, and with Meldola a new interest was a fresh opportunity for close study. In 1873 we find him back at the Royal College of Chemistry, by then transferred to South Kensington, as private assistant to Dr. Frankland, and later as demonstrator in the advanced students' laboratory. He also conducted a special course of practical organic chemistry for teachers and became lecturer on chemistry at St. Mark's College, Chelsea.

Being attracted by the study of spectrum analysis he also served for a time as assistant to (Sir) Norman Lockyer, with whom he worked for about three years studying the application of physics and chemistry to astronomical problems. He also acquired during this work a considerable knowledge of photography which just at that time was undergoing the development due to the introduction of the gelatin-bromide emulsion and the invention of the dry plate.

Although since 1869 Meldola had contributed as many as twenty-three publications on natural history and entomological subjects, it was not until 1874 that his first two chemical papers appeared (with D. Tommasi) "On the Action of Trichloracetyl Chloride Upon Amines and Urea", published in the *Journal of the Chemical Society*. Meldola's correspondence with Darwin commenced about this time and was concerned with the question of mimicry in nature, natural selection, and mutation: it led to a warm friendship, made the easier, no doubt, through Meldola's being Secretary of the Entomological Society over the period 1876—80. This friendship with Darwin was very real, and undoubtedly had a great influence on Meldola's life and interests, as indeed can be said, too, of the remark-

able observations and work of the German naturalist Fritz Müller, who was then in Brazil and the records of whose work came early to Meldola through Darwin. It was, in fact, Charles Darwin who later proposed Meldola for the Fellowship of the Royal Society on grounds of his biological work: Meldola was elected a Fellow in 1886.

Within a comparatively few years Meldola had established a reputation as a careful and painstaking observer and experimentalist, and had become a popular figure in a wide circle of friends. When (Sir) Norman Lockyer found it impossible to take charge of the Royal Society's expedition to Camorta in the Nicobar Islands to observe the total eclipse of the sun on April 6th, 1875, his assistant, Raphael Meldola, was put in charge. A second party, under Dr. Schuster, went to Siam for the same purpose, and a third, under (Sir) Alexander Pedler, left India to join Meldola's expedition at Galle, on the way to Camorta. The description of the eclipse is given in the *Philosophical Transactions* for 1878. The arrangements were remarkably thorough, but soon after the eclipse had begun local cloud formation completely obscured the sun during the period of totality. Meldola was in charge of the quartz telescope for photographing the spectra of the corona and prominences of the sun. He came back by the "Enterprise" to Calcutta and returned to England, disappointed, but the proud possessor of important records of the initial and final stages of the eclipse, and with much to his credit for the admirable way in which all the arrangements had been carried through.

During 1876 Meldola was appointed lecturer on science at the Ratcliff School of the Coopers' Company, and continued his industrial connections, which had already extended over the past eight years, as chemical adviser to the firm of W. & W. H. Stead, Seed Crushers and Oil Refiners, of Liverpool. A lifelong friendship grew out of this business connection; Meldola and W. H. Stead spent many holidays together, both at home and abroad, visiting mutual friends and attending the meetings of the British Association at York, Southampton, and Southport in the years 1881—83. Both took pride in this friendship, which again revealed Meldola's attractive personality and showed how long visits and holidays spent with him left memories delightful to recall.

In 1877, to quote Meldola's own words: "I accepted an appointment in the laboratory of Messrs. Brooke, Simpson and Spiller, of the Atlas Works, Hackney Wick, manufacturers of coal tar colours. Here I had the excellent opportunity of prosecuting original research

and at the same time of becoming practically familiar with the manufacturing operations of one of the most complicated branches of chemical technology." It may be remarked here that this firm were the successors of Simpson, Maule and Nicholson, one of the earliest and most successful of the English colour firms, established mainly through the energy and ability of Edward Chambers Nicholson, who had been a pupil of Hofmann at the Royal College of Chemistry.

This second contact with chemical manufacture opened a new chapter in Meldola's life and determined the course of his future research in chemistry: moreover it aroused in him a keen interest in technology which he retained to the last. In the laboratory he devoted himself assiduously to the problems of his new occupation and at the same time acquired much first-hand information and experience on the manufacturing and business side of this industry. All who knew him at that comparative early period of his life, for he was then only about thirty years of age, remarked upon his energy, his clear and methodical way of proceeding in his work, and his scrupulous regard for accuracy of detail.

Meldola remained at the Atlas Works for close upon eight years. His quiet, unassuming manner, the breadth of his knowledge, his orderly mind, and his happy buoyant personality made him a popular figure both in the laboratory and in the works. His somewhat severe appearance, remarkable in so small a man, was soon forgotten as his whimsical sense of humour and ready wit came to be appreciated. Like so many of his race he was not unmindful of the significance of business affairs, but with him they seemed to provide merely another field for study. Certainly he made himself familiar with the business side of the dye industry, a circumstance which, later on, fitted him in no ordinary way to be Chairman of the Advisory Council of the Board of British Dyes Limited.

During Meldola's connection with the Dye Industry he was the author of more than twenty papers and other communications in scientific journals on chemical subjects, some thirteen on entomological subjects, two connected with astronomy, and more than twenty on miscellaneous subjects, which included observations on ancient earthworks and pre-historic remains in Britain and several reports on the East Anglian earthquake of 1884. During those eight years he also played an important part in founding the Essex Field Club (1880) of which he became the first President. He taught himself German, and in 1881—82, at Charles Darwin's suggestion, he translated, edited, and annotated Weismann's "Studies in the

Theory of Descent" to which Darwin wrote a preface. It would appear that Darwin was very anxious that Meldola should make this translation, and in one of his last letters, written but a few weeks before his death, on April 19th, 1882, Darwin expressed a wish to subscribe towards the cost of the work should any loss be incurred by Meldola himself.

On the biological side it will be appreciated that this period was for Meldola full of interest and activity, for he was busy defending and adducing fresh evidence in support of the mimicry hypothesis advanced by Fritz Müller; yet, on the chemical side his fertile and imaginative mind was busy with the problems of the dye works. Meldola was a remarkably good, clean, and precise experimentalist himself, and much of the chemical work he did with his own hands. Those who had the privilege of working with him in his later years at Finsbury Technical College could not fail to be impressed by his simple manipulative dexterity in the laboratory, particularly in handling small quantities of material at the bench. The way he assiduously purified his products, often only a few grams, checking each step by combustion analysis lest he be led astray in his conclusions, remains with them as an example of high patience and investigational attainment.

Meldola's chemical work over this period was largely of a skirmishing or pioneer kind; he showed true originality and made many important discoveries, which if followed up with vigour and imagination would have led to important advances in the colour industry. His work, however, received little notice in England, but played a considerable part in the development of the dyestuff industry in Germany. In order to appreciate this it is necessary to bear in mind that British industry was then paramount: German industrialists, encouraged by two successful European wars, were seeking a place in the industrial world, and to this end their Government had devoted a considerable part of the French indemnity, which had been paid in gold, to the furtherance of scientific and technical education. Moreover, in Britain chemistry of this kind received little attention at that time from academic institutions and the learned societies, whereas in Germany the situation was far more favourable. In these circumstances, after making a valiant attempt to follow up the brilliant start made by W. H. Perkin and develop a progressive dyestuff industry in this country backed by research, Meldola, sadly disillusioned and bitterly disappointed by the obtuseness of the British manufacturers, retired from the dyestuff industry

in 1885. It will be recalled that Perkin had retired in 1874 unable to face the necessary expansion of research on a large enough scale, for neither the capital nor the supply of trained organic chemists was forthcoming. Meldola's experience was to be that of A. G. Green who succeeded him at Hackney Wick. Green was probably more inventive in this branch of science than Meldola, and it seems certain that, had these two been adequately supported by finance and management, the history of the British dyestuff industry might have been very different.

In the early part of 1885 the City and Guilds of London's Institute sought to fill the vacancies at their Technical College at Finsbury caused by the appointment of Henry E. Armstrong and W. E. Ayrton to the chairs of chemistry and physics at their Central Technical College then opened at South Kensington. Both Raphael Meldola and his friend Sylvanus P. Thompson were among the applicants for the post of Principal of the Finsbury Technical College, or alternatively, the Chair of Chemistry in the one case and of Physics in the other. Sylvanus Thompson was appointed Principal and Professor of Physics and Raphael Meldola to the Chair of Chemistry in March, 1885.

The breadth of Meldola's knowledge and experience had already provided him with a wide circle of friends, and one of his charming characteristics was the depth to which these friendships grew. Sylvanus Thompson had already become a close friend since their meeting some twelve years earlier at the Royal College: it is easy, therefore, to understand how happy and mutually useful these appointments were. These two men worked together at Finsbury for the next thirty years, and at Meldola's death, shortly before his own, Sylvanus Thompson was moved to say: "*Better friend no man could desire. Better and truer colleague no man could ever have. In daily association with him as a teacher, his companion in many country walks and expeditions, I had innumerable opportunities of learning what a clear and well stored mind was his: how rich and many-sided was his nature; with what a wide outlook he was endowed.*" This is no fulsome statement: those who knew the sincerity of Sylvanus Thompson and the worth of Raphael Meldola subscribe to every word.

Installed as Professor of Chemistry, on the top floor of the Finsbury College, Meldola lost no time in securing the collaboration in research of Frederick William Streatfeild, who was already at the College as lecturer and demonstrator, and from early in 1886 pub-

lished work from Meldola's laboratory began to appear in their joint names. The happy release from frustration in industry coincided, in the same year, with his electon to the Fellowship of the Royal Society and his marriage to Ella Frederica, daughter of Dr. Maurice Davis.

There can be little doubt that teaching did not appeal to Meldola; nor for students was he a good lecturer. His rather forbidding appearance and somewhat incisive mode of speaking were against him in this, and his shortsightedness was a hindrance in recognising people. Moreover, his lectures were too condensed and too meticulously prepared; his true self was masked, his sense of humour and his lively wit, so evident in his own laboratory, were missing. He was a good conversationalist, always precise, using carefully chosen words and arranging the emphasis; he enjoyed a good story—indeed, with the little adjustments and embellishments he sometimes introduced, the story improved and he would tell it very well. Those who knew him at Finsbury in the early days have spoken of his apparent dual personality, and of his extraordinary ability to continue writing about one subject while talking vigorously about something quite different. His was a strangely compartmented mind.

Streatfeild and John Castell-Evans, both very human people admirably suited for their task of teaching, seemed to provide all that was necessary between Meldola and his students. Those three men were keenly alive to their duty and responsibility in this matter; yet each contributed differently. The result was that happy relation between students and staff which characterised Finsbury College and made its high reputation as a training centre for chemists. Although Meldola kept rather in the background as regards actual teaching, lecturing only to the advanced students on organic chemistry, he was earnestly interested in this side of his duties. At the British Association meeting in 1888 he considered the "Methods of Teaching Chemistry", and contributed to a discussion on "Technical Education in Chemistry" to the Society of Chemical Industry the following year.

Meldola had deeply at heart the advancement of organic chemistry in this country and was fired by the technical opportunities presented to the British colour manufacturers by chemical research; yet he was stung by their apathy and their indifference to the science upon which that industry is based. In an address to the Royal Society of Arts in May, 1886, entitled "The Scientific Development of the

Coal Tar Colour Industry ", he delivered a public warning against the decadence of the industry in this country through the ineptitude of the manufacturers in not recognising the part which science plays in their industry. Meldola was at that time much impressed by the commercial possibilities as well as by the scientific opportunities of the dye industry, and neglected no occasion for directing public attention to the fact that the manufacture of dyestuffs was essentially a scientific business and could only be developed successfully on that basis. But his warning and admonitions fell upon deaf ears: there was, in fact, nobody in authority in the administration, or elsewhere, who understood the situation or appreciated the significance of his words.

It is scarcely surprising that Meldola's chemical researches at Finsbury were, in the main, a continuation of his dyestuff work, although only from the purely scientific point of view. His interest in photography was also sustained, and those who worked in his laboratory many years later remember the row of large sealed glass tubes in which silver chloride, bromide, and iodide were kept in presence of excess of the corresponding halogen and also under air alone; they stood in a sunny window and each bore on the label the date 1888. One remembers, too, how Meldola would from time to time examine the contents of these tubes under the pocket lens which he always carried, and after consulting his notebook would shake the tubes vigorously and replace them in the window. His interest in this subject provided the theme " The Photographic Image " for his lecture to the Royal Institution in 1890; a series of Cantor Lectures on " Photographic Chemistry " at the Royal Society of Arts; and his book on Photography the following year. Nevertheless, while devoting much attention to these chemical subjects he actively continued his interest in other branches of natural science and took an increasing part in public scientific affairs. He was elected President of the Entomological Society in 1896 and to the Council of the Royal Society. In 1900 he was offered the decoration of the Legion of Honour of France, but the British Foreign Office refused him permission to accept the distinction.

Reviewing Meldola's life and work is rather like rotating a kaleidoscope containing as bright objects some three or four branches of science and other accomplishments. The patterns which these formed at his hands led to a remarkable diversity of publication, and there can be no doubt Meldola liked publication—it had a strong appeal and fascination for him. He was master of a clear, concise,

and simple style, and his broad approach to any problem, coupled with his orderly mind and insistence upon the importance of detail, enabled him to write upon many subjects with discernment and precision. He read widely, and although blessed with a retentive and accurate memory he nevertheless made notes and entries on cards which he filed for future reference. How these were classified we shall never know, but they included anecdotes, quotations, and amusing stories. In this way he was able at short notice to discourse or write upon a wide range of subjects. This intellectual diversity brought him in touch with men and women of nearly every profession who found behind his natural shyness and reserve real geniality, tact, and courtesy which made him a charming host, and brought many to the frequent informal gatherings at his home in Brunswick Square.

In addition to F. W. Streatfeild, who over a number of years worked in Meldola's laboratory and was his confidant in such matters, recruits for research were drawn from students who had completed their final year in chemistry. Generally only one, sometimes two, worked in Meldola's laboratory and then only for about two years, so he had no opportunity to build up a team of research workers; indeed, it is doubtful whether he could have done so with all his other interests and activities. But he was very proud of the later achievements of those who had passed through his laboratory.

The work in Meldola's laboratory was exacting, but the training excellent, and here one met him in quite a different way. Whatever he put his hand to he did with zest and concentration. At the outset he made a full, clear, and frank statement of what he wanted to do, and an equally frank statement of what he expected of his assistant, and never referred to the latter subject again. In times of exciting activity, as during the early nineteen hundreds, there was a recognised daily routine comprising one complete combustion analysis, two nitrogen determinations by the method of Dumas with the use of a Sprengel pump, the preparation and purification of the materials used, the characterising of new substances, the keeping of clear and detailed records of everything made, purified, and analysed, and an evening letter to the Professor should he not be coming the next day. Gaps caused by absence were bridged by a brisk exchange of post-cards and letters, sometimes by closely following postal deliveries; sometimes one card extended or cancelled a card of the same date. All this certainly inspired the young recruit with enthusiasm, kept him very busy, and made him an accurate worker. In addition, for

in those days absolute alcohol was difficult to come by, all alcohol used was recovered and purified for further use. This was a permanent feature of Meldola's laboratory and meant far more to him than the value of the alcohol recovered. He was very wroth at the excuse made about that time by the dyestuff manufacturers that the difficulty of procuring and freely using supplies of alcohol at reasonable prices for industrial purposes, due to excise restrictions, lay at the root of the failure of the British dyestuff industry. He knew otherwise, and in 1904 willingly gave evidence before the Departmental Committee enquiring into the decline of the industry and spoke strongly of the ignorance and indifference to chemical research of those in charge as being the prime cause of failure.

As showing Meldola's activity during the first twenty years at Finsbury Technical College, one may quote from his own records of having published seventy-five papers on chemistry, twenty-five lectures and addresses, eighty-five reports and reviews, and close upon a hundred publications on a great variety of subjects, mainly natural history. For one who possessed so orderly a mind, and who lived and worked intensely in so methodical a manner as he imposed upon himself, it is surprising how much he admired the way of life of the French, seeing in their country the charm of freedom of thought and expression which he held dear yet could not emulate: next to his own country, England, he held France in the highest esteem.

There is no evidence that Meldola had any particular interest in the arts, although he was fond of string music and with his wife frequently went to concerts. He was, however, fond of quoting poetry, and would recite long passages from the "Ingoldsby Legends": the one entitled "The Knight and The Lady" was a favourite with him. An odd little smile would creep over his face on these occasions. The theme, the style, and the moral always amused him: such was his temperament. His humour may be exemplified further by a remark made to one of his assistants who travelled whenever possible by steam-boat from Cadogan Pier, Chelsea, to Old Swan Pier, London Bridge, and walked from there to the College. Meldola, feeling perhaps somewhat lost among the many preparations coming forward, said with a chuckle: "Have you considered, in the event of your getting drowned on your way here, or home, how much it would add to my distress to find that I could not readily identify all these substances through their not having been adequately labelled and put in their proper order?"

Meldola was a good chairman, tactful and judicious; he was also a popular and effective speaker at public and scientific gatherings. In 1901 he lectured at the Royal Institution on his favourite subject, "Mimetic Insects"; in 1904 his book entitled "The Chemical Synthesis of Vital Products" was published; in 1905 he gave a course of lectures at the Royal Institution, of which he had been a member since 1885, on "Synthetic Chemistry", and as President of the Chemical Society during 1905—07 his first address, entitled "The Living Organism as a Chemical Agency", was a review of some of the problems of photosynthesis by growing plants; on the second occasion, in a forthright address, he directed attention to "The Position and Prospects of Chemical Research in Great Britain". In 1907, at the instigation of the Chemical Society of France, he was once more offered the distinction of the Legion of Honour, and strangely enough the British Foreign Office once more declined to allow him to accept it. Naturally this troubled Meldola a good deal as he felt it was both an affront to his French colleagues and a sad indication of the indifference to science in official circles in this country.

In 1907 and 1908 Meldola was president of the Society of Dyers and Colourists in succession to W. H. Perkin, and in his presidential address at Bradford he told the story of the rise and early development of the British colour industry, the tragedy of which still lay heavy in his heart. This address, with Meldola's obituary notice of William Henry Perkin, published in the *Proceedings* of the Royal Society in 1907, provides a masterly summary of the position at that time. In the same year, Meldola gave an inaugural address to the School of Pharmacy on "The Scientific Training of the Pharmacist". As President of the Society of Chemical Industry in 1909 he again spoke on the subject of "Education and Research in Applied Chemistry". In these and in many other ways Meldola played a prominent part in scientific circles and in public affairs: it was strenuous, but he enjoyed it, hoping always that he would stand the strain. In all these preoccupations he was ably supported by his very charming wife; she was his inspiring companion, his devoted secretary, and his best friend. Like so many of the highly intelligent people of his race he was intensely patriotic, and ever anxious to advance science, industry, and the arts of his country in all possible ways, and in these endeavours he did not spare himself.

On the occasion of Meldola's Herbert Spencer Lecture in 1910

the University of Oxford conferred upon him the honorary degree of Doctor of Science. This was his first academic recognition and it gave him great pleasure, especially when he learned that it was the outcome of a memorial signed by all the scientific men of the University who were acquainted with his work. In the following year he received the LL.D. degree of St. Andrew's University, and in 1913 the Royal Society awarded him the Davy Medal.

Meldola was at the height of his fame at this time, and the reception which he and Mrs. Meldola gave at the Princes Galleries in London on July 4th, 1911, on the occasion of their silver wedding anniversary, provided ample evidence of his wide popularity. It was a brilliant occasion, attended by a large company of distinguished friends not only in science but in many other walks of life: the Duchess of Sutherland and the Countess of Warwick were present and many other gay and delightful people. On occasions of this kind Meldola lost much of his shyness and self restraint; he was a perfect host, beaming with pleasure, popular with everyone and thoroughly enjoying the presence of his many friends.

Having been elected to the presidency of the Institute of Chemistry in 1912, it fell to Meldola in the following year to give his first presidential address at a time when that Institute was embarking upon a scheme for building its own headquarters in Russell Square, and when the questions of status and prestige of its Fellows and Associates were being examined. All this brought more than the usual duties to the President, but his election was a wise choice for he brought to their deliberations a wide experience and a strong desire to be constructive. In his presidential address in 1913 he referred to the agitation in the chemical profession some thirty-six years previously, which had given rise to the Institute's formation in 1877 and confessed that until recently he had been indifferent to the movement, but had since changed his view, recognising there was a public mission to fulfil which could best be done by a corporate body of professional men. His period of office, which lasted until his death, was marked by statesmanship and good counsel. He did much to harmonise the examinations of the Institute with those of the Universities, and strove to bring about the adoption of some concordant scheme which would be of mutual advantage to the educational institutions of this country and the professional bodies, and so secure a greater measure of unity in the profession.

In 1914 Meldola served for a second time on the Council of the Royal Society and was elected a Vice President. He was at this

time much overworked, and although he was not actually ill his wiry physique was showing strain, and he was frequently indisposed. In August of that year war broke out, and this country was in a very difficult situation because in many important sections of our smaller industries manufacture had been allowed to give place to the mere buying and selling of foreign goods. Meldola had long been critical of this state of affairs, particularly as affecting chemistry, and at once convened meetings to consider the question of supplies of laboratory requirements. As chairman of some of these he did much to tide over the dilemma in which all chemical work had been placed through the cessation of foreign supplies. He successfully urged the Board of Trade to set up a committee to deal with the question of the supply of chemicals and became a member of the Advisory Committee appointed for the purpose in 1914: he served also on the Advisory Concil set up under the Order in Council of July 28th, 1915, to frame a scheme for the " Organisation and Development of Scientific and Industrial Research ". On January 20th, 1915, there was published in *The Times* a strong letter from Meldola protesting against the formation by the Government of a national co-operative company, British Dyes Limited, upon the directorate of which scientific chemistry was not represented. This lamentable attempt by the Government to deal with a vast industrial failure was criticised effectively in his last Presidential Address to the Institute of Chemistry in March, 1915. In July of that year he became Chairman of the Advisory Council of British Dyes Limited, a position which caused him a great deal of anxiety, yet his past experience and knowledge of the industry qualified him in an exceptional manner for the task. Thus fully occupied, and with failing strength following an operation in the spring, he found the duties laid upon him difficult to sustain. But his patriotism, his desire to help his country in those days of confusion and stress, brought more than his strength could support. By the autumn he was a weary man, soon a spent force, and he died suddenly on November 16th, 1915.

To his memory there is a portrait in oils by Soloman J. Soloman, R.A., in the apartments of the Royal Society, and another by the same artist in the Royal Institute of Chemistry, where there is also the bronze bust of Meldola which was removed from the Finsbury Technical College when it was closed down, and a miniature by Lionel Heath, presented by Mrs. Meldola for safe keeping. In addition, the Society of Maccabæans established a Memorial Fund, admin-

istered by the Royal Institute of Chemistry, for the award of a Meldola Medal.

An attempt has been made in these pages to give an account of the life and work of one of the outstanding personalities of the time 1870—1915, not only in the realms of chemistry, education, entomology, and technology, but in the struggle to secure an appreciation of science in industry and in public life. In addition to personal knowledge and experience of the man himself, the writings of his contemporaries have been freely drawn upon, particularly Professor Poulton's obituary notice and the memoir by Sir William Tilden, both written for the Royal Society ; likewise the excellent compilation of reminiscences by those who knew him which form the book " Raphael Meldola ", edited by James Marchant and published in 1916, and the address by Sir James J. Dobbie who succeeded Meldola as President of the Institute of Chemistry in that year.

In Meldola's life and work one perceives a remarkable duality : a striving after knowledge for the sake of gaining knowledge, and a strong desire to put it to practical purpose : a man who trod narrow paths of investigation himself notwithstanding his broad knowledge of the sciences and a wide experience : by disposition, too, he was both severe and humorous. At this distance of time it is perhaps difficult to appraise the full significance of his contributions to science; our standards of comparison change and it becomes impossible to recapture the conditions and the environment. Measured by current ideas, and with our vastly improved facilities, it may seem that Meldola's contributions to science were somewhat meagre : yet his full and purposeful life made an important contribution, particularly in chemistry, more particularly in industrial chemistry, through his persistent and successful efforts to bring scientific knowledge to industrial use, and in promoting science in the public esteem. He was essentially an industrial chemist, much before his time in an unappreciative era, from which, even now, this country is but slowly moving.

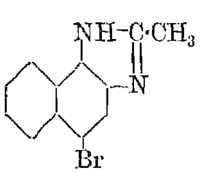
Meldola's Chemical Work.

Until he joined the firm of Brooke, Simpson, and Spiller in 1877, Meldola's contributions to chemistry were slight. From that time onward, however, until the end of his life, chemical research was one of his constant activities, and he was a regular contributor of papers

to the *Journal of the Chemical Society*, besides publishing occasionally in the German *Berichte*, the *Chemical News*, and other journals. Of necessity his researches were concerned at first with matters of interest to a firm of dye manufacturers. The firm appears to have followed an enlightened policy concerning publication, allowing Meldola a freedom in this respect which was rarely accorded in subsequent years to other workers in the field of dye chemistry. It is clear from his publications from the Hackney Wick works, during the 1877—85 period, that Meldola was exploring pretty widely, feeling his way into the chemistry of naphthalene, then just starting to interest dyestuff chemists, studying the chemistry of azo-compounds, and making exploratory experiments suggested to his mind by the work of his contemporaries. The problems which he encountered during these years served as a basis for the researches which he subsequently pursued at Finsbury. Indeed, he never strayed far from the chemistry of benzene and naphthalene or took inspiration from any other source for his experimental work, although his writings and addresses show that he read widely and thought more deeply than the restricted range of his researches would suggest. His opportunities for practical research at Finsbury Technical College were, it must be remembered, very limited, for there were no research students, and he had to rely for collaborators on other members of his staff and generally but a single research assistant who stayed only for a brief period, and left as he was becoming useful.' In these circumstances it is not surprising that the period at Finsbury is not characterised by the earlier originality, but rather by dogged perseverance in selected lines of investigation.

Meldola's earliest paper from Messrs. Brooke, Simpson, and Spiller's works was concerned with the constitution of the products of halogenation of α-acetnaphthalide. At this time some derivatives of naphthalene, such as α-nitronaphthalene, α-naphthylamine, and β-naphthol were becoming available on a commercial scale, and chemists were curious to know how these compounds behaved towards reagents producing further substitution, since the number of isomers possible was much greater than with benzene derivatives. Both iodination and, more fully, bromination, were studied. The homonuclear orientation of the mono- and di-bromoacetnaphthalides was proved, and incidentally it was found that the first effect of bromine on mono-(4-)iodoacetnaphthalide is to displace the iodine. During this work the orientation of 1 : 4-, 1 : 3-, and 1 : 2-dibromo-

naphthalenes was confirmed, the last being obtained from β-acetnaphthalide by bromination and replacement of the amino-group by bromine, confirming the substitution of β-naphthylamine derivatives in the 1- and not in the 3-position. 1 : 4-Dibromonaphthalene was also identified as a product of bromination of naphthalene itself (*Ber.*, 1878, **11**, 1904; 1879, **12**, 1961; *J.*, 1883, **43**, 1). These results were subsequently made use of in a study of the bromination of 2- and 4-nitroacet-α-naphthalides, which were shown to give respectively the 4- and 2-bromo-derivatives. 2-Bromo-4-nitroacet-α-naphthalide was shown to be decomposed by boiling sodium hydroxide solution to 2-bromo-4-nitro-α-naphthol. It was also shown that the product of nitration of 4-bromoacet-α-naphthalide must be the 2-nitro-derivative, since on reduction the product gave an *anhydro-base* (methylnaphthiminazole), a type of compound to which Meldola subsequently gave a good deal of attention.

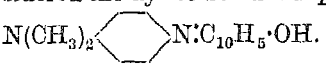


From the two bromonitroacet-α-naphthalides Meldola prepared, by eliminating the amino-group and reducing the nitro-group, the hitherto unknown 3-bromo-1-naphthylamine and 1-bromo-3-naphthylamine. The acetyl derivatives of these were further brominated to give two dibromonaphthylamines, the second bromine entering the unsubstituted ring in both compounds, but its precise orientation could not at that time be determined. During this work Meldola also made a large number of iodonaphthalene derivatives (*J.*, 1885, **47**, 497).

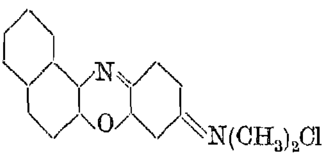
On a few subsequent occasions Meldola made some contributions to naphthalene chemistry. With Streatfeild he prepared some 1 : 8-disubstituted derivatives starting from 8-nitro-1-naphthylamine (*J.*, 1893, **63**, 1054) and with Hughes he studied the action of fuming nitric acid on dibromo-α-naphthol (*J.*, 1890, **57**, 393). Meldola and Hughes believed, on the strength of analytical results, that their main product was a bromo-indone, but Liebermann and Schlossberg (*Ber.*, 1899, **32**, 546) showed that it was 2-bromo-α-naphthaquinone, whilst a by-product which Meldola and Hughes considered might be the unknown 1 : 8-naphthaquinone (*J.*, 1890, **57**, 632) proved to be ββ′-dinaphthaquinone, since by reduction with zinc dust it gave ββ′-dinaphthyl (*Ber.*, 1899, **32**, 868, 2906).

The discovery with which Meldola's name will always be associated in dyestuff history is that of the first oxazine dye, commonly known, first in Germany and then generally, as Meldola's blue. Witt had

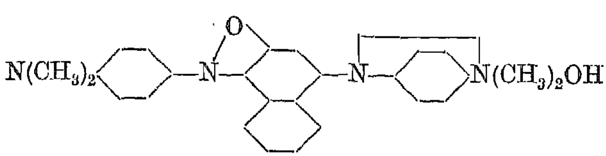
shown that a colouring matter could be obtained by heating nitrosodimethylaniline hydrochloride with *m*-tolylenediamine, and Meldola conceived the idea of substituting a phenol for the *m*-diamine. As typical phenols he chose, besides resorcinol, α- and β-naphthols. When the last was heated in acetic acid solution with nitrosodimethylaniline hydrochloride there was obtained a blue colouring matter, crystallising as its hydrochloride. Meldola considered the dye to be an indophenol and gave for the base the formula



Meldola apparently did not think it would be of much value as a dyestuff; he speaks of it as dyeing silk a dull violet and wool a deep indigo blue (*J.*, 1881, **39**, 37), but he says nothing of dyeing it on mordanted cotton. However, the German dyestuff firms soon realised the value of the new dyestuff and before long several of them were manufacturing it under such names as Neublau, Naphthalenblau, Echtblau, and Baumwollblau, no patent having been claimed by Meldola or his firm.

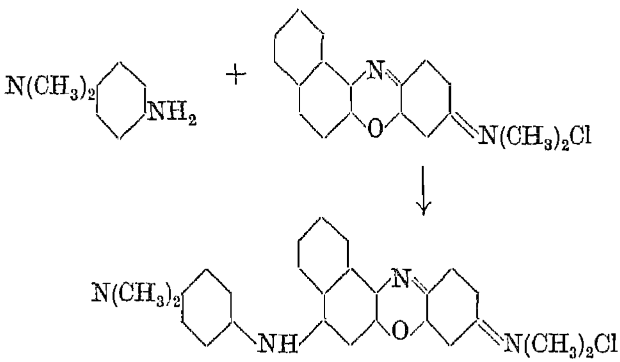


It was first suggested by Nietzki and Otto (*Ber.*, 1888, **21**, 1744) that Meldola's blue is an oxazine having the annexed formula, they having prepared the unalkylated parent dye from quinone-dichloroimide and β-naphthol. A little while later Witt pointed out that the several manufactured brands of Meldola's blue differed considerably in shade, and he isolated from the product of reaction of β-naphthol and nitrosodimethylaniline a colour base which from its analysis was derived from 1 mol. of β-naphthol and 2 mols. of nitrosodimethylaniline. He suggested for this product the structure:



and it was left to Hirsch and Kalckhoff, two chemists working at the Kirkheaton Colour Works, Huddersfield (*Ber.*, 1890, **23**, 2992), finally to clear the matter up. The last stage of the formation of Meldola's blue is the oxidation of the dihydro-oxazine to oxazine by nitrosodimethylaniline, with formation, by reduction of the latter, of *p*-aminodimethylaniline. It was shown that all primary

amines interact with Meldola's blue by condensation and oxidation to give amino-derivatives, thus :

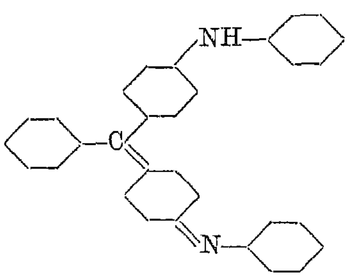


Consequently Meldola's blue is liable to contain more or less of the last product, which was in fact manufactured as an individual dye-stuff, being bluer in shade than Meldola's blue.

Meldola himself followed up his discovery in another direction, making another opening for others to win the reward. Wanting to obtain a sulphonic acid of his new blue dye, and failing to get this by direct sulphonation, he thought of preparing a nitroso-β-naphtholsulphonic acid and condensing this with dimethylaniline. The nitroso-β-naphtholsulphonic acids were then unknown, but he prepared one from what is now know to be β-naphthol-6-sulphonic acid, and published the details (*J.*, 1881, **39**, 40). This product, in the form of its iron complex, soon became an important printing green which is still manufactured in large quantities as naphthol green B (G.P. 28065/1884). When reduced it gave 1-amino-2-naphthol-6-sulphonic acid which was introduced and used as a photographic developer under the name " eikonogen " (see Meldola, *J. Soc. Chem. Ind.*, 1889, **8**, 958).

Another discovery of Meldola's, one which was exploited by his firm, was that of the first alkali green, a sulphonated dyestuff dyeing wool from an alkaline or neutral dye bath. The discovery was reported by Meldola in a paper in the *Berichte* (1881, **14**, 1385) but the new dye had already been shown at the Paris Exhibition in 1878 under the name " viridine ", by Messrs. Brooke, Simpson, and Spiller. A fuller account of the discovery was given to the *Journal of the Chemical Society* (1882, **41**, 187). The dye was obtained by heating benzyl chloride and diphenylamine together, oxidising the

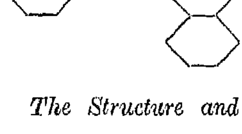
product with arsenic acid, and then sulphonating. Meldola's discovery coincided very closely with the discovery of a green basic dye by Doebner (malachite green) by heating dimethylaniline with benzotrichloride in presence of a metal chloride (G.P. 4322 of 26.2.1878), which dye Doebner identified (*Ber.*, 1878, **11**, 1236) with that obtained in 1877 by Otto Fischer by oxidising the condensation product of dimethylaniline and benzaldehyde (*Ber.*, 1877, **10**, 1624). Meldola suspected that his dye, like malachite green, must belong to the triphenylmethane series, and, with this clue to work on, found that he owed its discovery to the presence of benzylidene chloride, $C_6H_5{\cdot}CHCl_2$, and benzotrichloride, $C_6H_5{\cdot}CCl_3$, in the benzyl chloride which he had used. He proved the point by direct synthesis of his dye from benzylidene chloride and benzotrichloride, preparing and analysing the mono- and di-sulphonic acids. His dye was a sulphonated derivative of the dye base of the formula given, and strictly analogous to Nicholson's sulphonated phenylated rosanilines. Meldola's discovery was the forerunner of many sulphonated dyes of the malachite green type and was eventually superseded as a commercial article. It may have been the discovery of the constitution of his "viridine" which led him to experiment on the effect of heating rosaniline with other aromatic amines besides aniline, for it was at about this time that he discovered the β-naphthylated rosanilines, which on sulphonation gave soluble dyes which not only dyed wool from an alkaline bath but also dyed cotton from an acetic acid bath a bright blue shade (*Chemical News*, 1883, **47**, 133). Dyes of this constitution were manufactured by Messrs. Brooke, Simpson and Spiller under the name of alkali blue XG and by several German firms under such names as brilliant cotton blue, isamine blue, and direct blue.



Meldola did not follow up his brief incursion into the field of triarylmethane chemistry, but he was at about the same time engaged on a planned study of azo-dyestuffs. With the evidence of his work before us we can see what opportunities were missed for developing this field in Britain. Had Meldola's work on naphthalene chemistry been pursued more intensively in parallel with his studies of azo-compounds, had a greater supply of trained

chemists been available to assist him, many of the important new dyes which were discovered in Germany would have originated here.

Meldola was seeking at this time improved methods for obtaining complex azo-compounds containing two or more azo-groups, and he invented a method which quickly proved to be one of the greatest importance. This consisted in diazotising a nitroaniline, coupling the diazo-compound with an amine or phenol, and then reducing the nitro-group to form an aminoazo-compound which could be itself diazotised and coupled with an amine or phenol. The essential novelty in Meldola's process was the discovery of a method for reducing the nitro-group of the nitroazo-compound without at the same time reducing the azo-group, for which purpose he used ammonium sulphide. An alternative method for achieving the same objective was already known, namely, to start with a diazo-compound containing an acetamido-group, from which the acetyl group could be removed by hydrolysis after coupling, thus obtaining the required aminoazo-compound. But diazo-compounds such as *p*-acetamidodiazobenzene are weak couplers and not so generally useful as, for instance, *p*-nitrodiazobenzene which is a very active coupling component, and Meldola's development was, therefore, of considerable importance. *p*-Nitroaniline, which was to become an important dye intermediate, was then so unfamiliar that Meldola felt it necessary to give a full description of its preparation (*J.*, 1883, 43, 425). By his process Meldola made a range of dyes by coupling diazotised *p*-nitroaniline with diphenylamine, dimethylaniline, and other bases, reducing the nitro-group, again diazotising, and coupling with β-naphthol or its (6-)sulphonic acid, or with phenol or resorcinol; other dyes were made in which both coupling components were phenols or naphthols. The papers describing this work contain many observations significant to the practical chemist. When *m*-nitroaniline was used instead of *p*-nitroaniline, it was not found possible to reduce the *m*-nitro-group of the azo-compound selectively, the molecule splitting by reduction of the azo-group. The abnormal properties of azo-compounds formed when β-naphthylamine was coupled with a diazo-compound were noted. These could not be diazotised but formed nitroso-compounds with nitrous acid, and Meldola suggested tentatively a structure for them of the type illustrated (*J.*, 1885, 47, 107, 657).



The Structure and Isomerism of Diazoamino-Compounds.—The

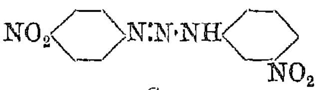
researches on diazoamino-compounds were carried out in collaboration with Streatfeild during the period 1885—90. When the work started it was not known for certain whether the compounds obtained by the action of diazo-compounds of *m*- and *p*-nitroaniline were true diazoamino-compounds or abnormal aminoazo-compounds such as those formed by β-naphthylamine. A thorough investigation was made of the diazoamino-compound from *p*-nitroaniline, which was found to be acid in character, forming metal salts which could be isolated and analysed. It was ethylated without difficulty, and, when the ethyl derivative was heated with concentrated hydrochloric acid, *p*-nitroethylaniline and *p*-chloronitrobenzene were obtained. This result, combined with the fact that the original compound gave only *p*-phenylenediamine on reduction, confirmed the diazoamino-constitution (*J.*, 1886, **49**, 624).

It had been shown by Griess that some unsymmetrical diazoamino-compounds which would be expected to have two isomeric forms showed in fact only one form; thus the same product was obtained from diazotised aniline and *p*-bromoaniline as from diazotised *p*-bromoaniline and aniline. Which was the correct structure, *A* or *B*?

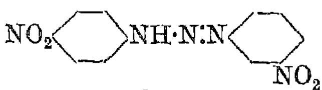
A.

B.

Meldola and Streatfeild attacked this problem by making a thorough study of 4 : 3′-dinitrodiazoaminobenzene, obtainable from diazotised *p*-nitroaniline and *m*-nitroaniline, or from diazotised *m*-nitroaniline and *p*-nitroaniline. It was shown that the compound, whichever way it was prepared, behaved as if it were a mixture of both possible forms, *C* and *D*.



C.



D.

When heated with concentrated hydrochloric acid in a sealed tube it gave *m*- and *p*-nitroanilines with *m*- and *p*-chloronitrobenzenes; when decomposed by dilute hydrochloric acid it generated a diazo-compound which coupled with β-naphthol giving a mixture of *m*- and *p*-nitrobenzeneazo-β-naphthols. The *N*-ethyl derivatives were then investigated, being prepared (i) by ethylating the diazoamino-compound, (ii) by combining *p*-nitrodiazobenzene with *m*-nitroethylaniline, and (iii) by combining *m*-nitrodiazobenzene with

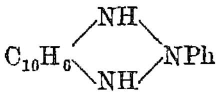
p-nitroethylaniline. Whilst the products of (ii) and (iii) behaved as distinct chemical entities, decomposing with dilute acid to give the starting materials, the product of (i), like the diazoamino-compound from which it was prepared, behaved like a mixture. Yet Meldola and Streatfeild became convinced that the product of (i) was not a mixture but a distinct isomeric form of the *N*-ethyldiazoamino-compound, largely on the ground of physical properties, which were different from those of a mixture of the products of (ii) and (iii). A number of other examples of asymmetric diazoamino-compounds were studied, such as that in which the amine components were *p*-nitroaniline and *p*-bromoaniline. The work was made more difficult by the circumstance that sometimes symmetrical diazoamino-compounds were obtained instead of the asymmetrical. Thus when it was attempted to form a diazoamino-compound from diazotised *m*- or *p*-nitroaniline and *p*-chloroaniline, much dinitrodiazoamino-benzene was formed. This could only be attributed to the ready decomposition of the asymmetrical diazoamino-compound in two ways :

$$\mathrm{X{\cdot}NH{\cdot}N{:}NY \longrightarrow X{\cdot}NH_2 + Y{\cdot}N{:}NCl \text{ and } Y{\cdot}NH_2 + X{\cdot}N{:}NCl}$$

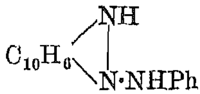
giving products from which X·NH·N:NX and YNH·N:NY could be formed. In spite of these difficulties several examples were found of *N*-alkylated asymmetric diazoamino-compounds apparently existing in three isomeric forms, two obtained from the *N*-alkylated anilines and the third by alkylating the asymmetric diazoamino-compound. It was surmised at one time that the last form was dimeric, this idea being supported by quantitative coupling experiments which pointed to its being composed of equimolecular proportions of X·NEt·N:NY and X·N:N·NEtY, but molecular weight determinations by Raoult's method disproved the proposition. The problem was left in an unresolved state. This work on diazoamino-compounds had timely importance for those who were developing the applications of diazo-compounds, and constitutes one of the first studies of a tautomeric system.

o-*Amino- and* o-*Hydroxy-azo-compounds.*—Chemists were puzzled by the abnormal properties of azo-compounds containing an amino- or hydroxyl group in ortho position to the azo-group, and Meldola took an active part in the experimental attack on this problem. The abnormal properties were especially marked in azo-compounds obtained by coupling diazo-compounds with β-naphthol or β-naphthylamine. Indeed Zincke was at pains to prove that benzene-azo-β-naphthylamine was not a diazoamino-compound, by showing

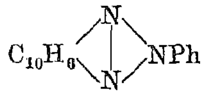
that it was different from the diazoamino-compound from diazotised β-naphthylamine and aniline, with which, on the evidence, for example, of much of Meldola's work, it would have been identical had it been a diazoamino-compound (*Ber.*, 1885, **18**, 3133). Such compounds as benzeneazo-β-naphthylamine could not be diazotised with nitrous acid but, according to Meldola (*J.*, 1884, **45**, 117), formed nitroso-compounds. He was inclined to formulate them as



(I.)



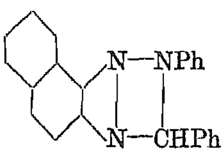
(II.)



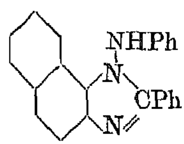
(III.)

(1), but Zincke favoured (II), and called the compounds hydrazo-imides since on oxidation they gave azo-imides (III). It was agreed that they could not contain an amino-group, until Zincke and Lawson (*Ber.*, 1887, **20**, 2897) showed that diazotisation could be affected in acetic acid solution with nitrous fumes. Meldola and East diazotised *m*-nitrobenzeneazo-β-naphthylamine in the same manner and by boiling the product with acetic acid converted it into *m*-nitrobenzeneazo-β-naphthyl acetate (*J.*, 1888, **53**, 460). This direct replacement of the diazo-group by the acetoxy-group was Meldola's own discovery (*ibid.*, p. 601). Later Meldola and Hughes prepared acetyl derivatives of *o*-, *m*-, and *p*-nitrobenzeneazo-β-naphthylamines, which were found to be unaffected by nitrous acid, but it was admitted that this observation threw no further light on the constitution of the azo-compounds (*J.*, 1891, **59**, 372).

Meldola also prepared benzylidenebenzeneazo-β-naphthylamine by coupling diazobenzene with benzylidene-β-naphthylamine (*J.*, 1890, **57**, 328) and made the interesting observation that when heated, alone or better in acetic acid, it was converted into a stable, colourless compound identical with one which had been obtained by Goldschmidt and Rossell (*Ber.*, 1890, **23**, 487) by the action of benzaldehyde on benzeneazo-β-naphthylamine, and was formulated as the dihydrotriazine (I). Meldola and M. O. Forster prepared a large number of such compounds and studied their properties



(I.)



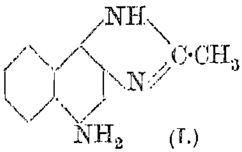
(II.)

(*J.*, 1891, **59**, 678). They could be alkylated, and when the compound from *m*-nitrobenzeneazo-β-naphthylamine was reduced with tin and hydrachloric acid it was found to give *m*-phenylenediamine and 2-phenylnaphthiminazole. More than thirty years later these observations caused O. Fischer to doubt the constitution assigned to the compounds, and he showed that they are undoubtedly anilino-iminazoles of type (II) (*J. pr. Chem.*, 1922, **104**, 102).

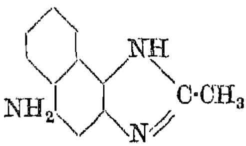
The constitution of benzeneazo-β-naphthol was under examination at the same time, the question being whether it did or did not contain a hydroxyl group. Meldola and East showed that *m*-nitrobenzeneazo-β-naphthol could be acetylated to the same compound as was obtained by diazotising *m*-nitrobenzeneazo-β-naphthylamine in acetic acid, presumably but not certainly the *O*-acetyl compound. Weinberg claimed to have ethylated the azo-compound, but when Meldola and G. T. Morgan examined a specimen of his preparation they found it to contain much unchanged benzeneazo-β-naphthol. They found it impossible to effect complete ethylation (*J.*, 1889, **55**, 603). With E. M. Hawkins (*J.*, 1893, **63**, 923) and with Burls (*J.*, 1895, **67**, 930) Meldola studied the reduction of benzeneazo-β-naphthyl acetate and other azo-derivatives of β-naphthol. If the acetyl group were attached to nitrogen, acetanilide should be formed; if to oxygen, acetamido-β-naphthol, by isomeric change of 1-amino-β-naphthyl acetate. In fact the results were inconclusive, both products being formed. At this time Meldola seems to have formed the sound opinion that the constitution of tautomeric substances such as the azonaphthols cannot be determined by chemical means, since one form can readily pass into the other during any chemical reaction. This same problem has continued to attract chemists at intervals, and as recently as 1935 Kuhn and Bähr concluded on spectroscopic evidence that both 1-benzeneazo-2-naphthol and 2-benzeneazo-1-naphthol exist mainly in the quinone-hydrazone form (*Annalen*, 1935, **516**, 143). The properties of these *o*-amino- and *o*-hydroxy-azo-compounds can also be accounted for by assuming hydrogen bonding between the amino- or hydroxyl group and one of the nitrogen atoms of the azo-group. This assumption was, of course, outside the realm of speculation in Meldola's time.

Anhydro-bases or Naphthiminazoles.—Another class of compound with which Meldola concerned himself for many years was that represented by anhydro-compounds formed from acyl derivatives of *o*-diamines, now termed iminazoles but at that time variously called amidines (to which they are related), ethenyldiamines, etc. With

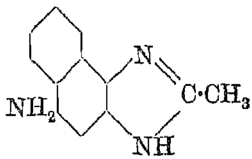
Streatfeild he obtained, by reducing 2 : 4-dinitroacetnaphthalide with tin and hydrochloric acid, a compound supposed to be the aminonaphthiminazole (I) (*J.*, 1887, **51**, 691), and later with Phillips (*J.*, 1899, **75**, 1011) submitted it to further examination, acetylation, diazotisation and coupling with diazo-compounds. Then it was discovered that this compound was markedly different from the product obtained by Markfeldt (*Ber.*, 1898, 31, 1174) by reducing 2 : 4-dinitroacetnaphthalide with iron and hydrochloric acid instead of tin and hydrochloric acid. Analysis indicated isomerism of the two products. They gave different acetyl derivatives, different colours with diazobenzene, and different products when the amino-group was eliminated. The research was continued in collaboration with Eynon (*J.*, 1900, **77**, 1159) and Eyre and Lane (*J.*, 1903, **83**, 1185) and Meldola became convinced that, in some unexplained way, the two methods of reduction gave the tautomers (II) and (III).



(I.)

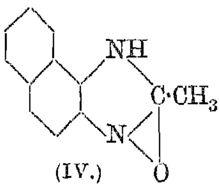


(II.)



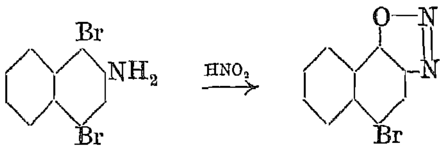
(III.)

Two of his own observations, however, contributed to the eventual solution of the problem; first that the compound obtained by tin reduction changed on further treatment with iron and hydrochloric acid to that obtained by Markfeldt; secondly, that the base obtained by the tin method gave on deamination a methylnaphthiminazole which adhered to water of hydration even when crystallised from aniline. Some years later the problem was solved by O. Fischer (*J. pr. Chem.*, 1907, **75**, 88) who on other grounds was convinced of the virtual tautomerism of the iminazoles. He showed that the product obtained by Meldola by tin reduction did not contain, as the latter supposed, water of hydration, but two hydrogen atoms less than the hydrate required and was in fact an incompletely reduced product to which he assigned the structure (IV). Reduction by iron and hydrochloric acid converted it into the true iminazole.



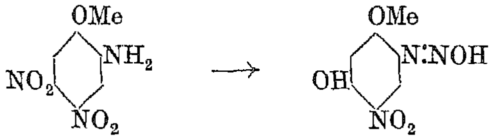
(IV.)

Displacement of Groups in Aromatic Compounds.—Meldola's researches, particularly in his later years, contributed considerably to our knowledge of the conditions governing the displacement of groups in aromatic compounds. His first observation of this kind occurred when he and Streatfeild diazotised 1 : 4-dibromo-2-naphthylamine and obtained 4-bromonaphthalene-2 : 1-diazo-oxide :

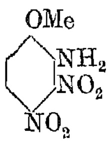


This was the first record of the displacement of halogen in the course of diazotisation, although Gaess and Ammelburg had observed the similar displacement of a nitro-group (*Ber.*, 1894, **27**, 2211). Meldola showed that chlorine could be displaced in the same way, and the reaction was later applied technically by German dyestuff firms who used it by diazotising chloronaphthylaminesulphonic acids to obtain diazo-compounds derived from 2 : 1- and 1 : 2-aminonaphthol-sulphonic acids (B.P., 6615, 1902; 16995, 1903; etc.), chlorine and sulphonic group both being displaced in alkaline solution.

The next observation on this subject records the replacement of a nitro-group para to an amino-group by hydroxyl when 4 : 5-dinitro-*o*-anisidine is diazotised, an additional point of interest being that the nitrous acid formed by the eliminated nitro-group could continue the diazotisation once it was started. In fact, a form of chain reaction had been discovered.



It was shown, for example, that nearly complete diazotisation could be achieved, slowly, using only about a quarter of the theoretically necessary quantity of nitrous acid, the eliminated nitro-group providing the remainder (Meldola and Eyre, *J.*, 1901, **79**, 1076). The isomeric 3 : 4-dinitro-*o*-anisidine showed interesting behaviour. When it was diazotised in acetic acid, the nitro-group ortho to the diazo-group was replaced by hydroxyl; in hydrochloric acid the same nitro-group was replaced by chlorine; but when sulphuric or nitric acid was used the nitro-group remained undisturbed (Meldola and Eyre, *J.*, 1902, **81**, 988). Another kind

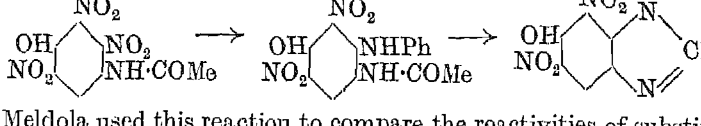


3 : 4-Dinitro-*o*-anisidine

of change occurred when 2 : 6-dinitro-*p*-anisidine was diazotised in mineral acid solution, the methoxyl group being demethylated and a 1 : 4-diazo-oxide formed. Further experiments with dinitroanisidines of different orientations showed that the conditions necessary for the displacement of a nitro-group or the demethylation of a methoxyl group were first that the affected group must be ortho or para to the diazo-group, and secondly that it must be adjacent to a nitro-group. Thus no displacement occurs when 3 : 5-dinitro-*o*-anisidine or 3 : 5-dinitro-*p*-anisidine is diazotised (Meldola and Hay, *J.*, 1907, **91**, 1474). An interesting sequel to this work is seen in a recent paper by B. B. Dey *et al.* (*Current Science*, 1946, **15**, 161) who observed that when 2 : 5-dichloro-4-nitroaniline is diazotised in hydrochloric acid the nitro-group is replaced by chlorine. Here there is no nitro-group, but chlorine, ortho to the affected group.

The work described above necessitated a considerable amount of research on the nitration of the acylated aminophenols and anisidines and the orientation of the products. In some of this work Meldola collaborated with the distinguished chemist Reverdin, of the University of Geneva, with whom he published two joint papers (*J.*, 1910, **97**, 1204; 1913, **103**, 1484). His research activities during the last few years of his life were concerned almost entirely with a study of the chemistry of these nitro-compounds, and led to some remarkably interesting papers. Much work was done with a trinitro-compound obtained by the action of fuming nitric acid on diacetyl-*p*-aminophenol (*J.*, 1906, **89**, 1935). This product was for some years believed to be 2 : 3 : 5-trinitro-*p*-acetamidophenol and is referred to as such in several papers, but in 1913 Meldola and Reverdin in a joint paper showed that in fact it is the 2 : 3 : 6-trinitro-compound. When methylated it gave a trinitro-*p*-anisidine isomeric with a compound obtained by Reverdin to which had been assigned the constitution 2 : 3 : 6-trinitro-*p*-anisidine; this latter proved, however, to be the 2 : 3 : 5-trinitro-compound (*J.*, 1913, **103**, 1484).

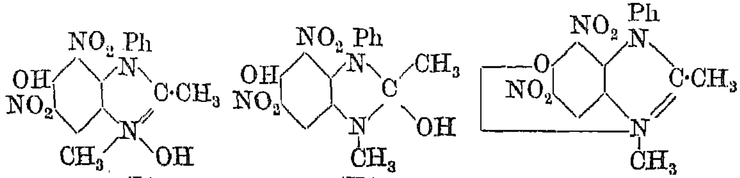
2 : 3 : 6-Trinitro-*p*-acetamidophenol reacted readily with primary amines, the 3-nitro-group being displaced, and the products were readily converted into iminazoles by dehydration. For example, aniline reacted as follows :



Meldola used this reaction to compare the reactivities of substituted anilines, including the three chloroanilines, bromoanilines, anisidines,

nitroanilines, aminophenols, and aminobenzoic acids, and α- and β-naphthylamines, by comparing the yields of iminazole obtained. In general the yields were between 80 and 100%, ortho-substituted anilines giving somewhat lower yields than the meta and para compounds. A striking exception was *o*-nitroaniline which did not react at all, although the *m*- and *p*-compounds gave 95% and 98% yields respectively. These results corresponded closely with Wedekind's observations in the reaction between picryl chloride and substituted anilines (*Ber.*, 1900, 33, 426). Of secondary amines which he examined only piperidine and dimethylamine reacted; diethylamine was quite inactive. It was clear that steric hindrance played a part in limiting this reaction (Meldola and Hay, *J.*, 1907, 91, 1474; 1908, 93, 1659). The trinitro-*p*-aminophenol, unlike its acetyl derivative, did not react in the same way with primary amines, nor was the 3-nitro-group displaced when the amine was diazotised, but a *p*-diazo-oxide was formed. In this compound, however, the 3-nitro-group was replaced by hydroxyl by boiling it with aqueous sodium acetate (*J.*, 1909, 95, 1378). The interesting observation was made that both 2 : 3 : 5- and 2 : 3: 6-trinitro-*p*-anisidines lost the 3-nitro-group on diazotisation, giving diazo-oxides; in neither reaction was there any tendency for the *p*-OMe group to be disturbed. In 2 : 3 : 5-trinitro-*p*-anisidine the 2-nitro-group was displaced by the action of primary amines; thus in both trinitro-*p*-anisidines the mobile nitro-group (apart from the special case of diazo-oxide formation) was that one having other nitro-groups both ortho and para to it. Meldola also discovered the mobility of the methoxyl group in 2 : 4-dinitro-1-methoxynaphthalene, which reacts with alkylamines to form 2 : 4-dinitro-1-alkylnaphthylamines (*J.*, 1906, 89, 1434).

The closing chapters of Meldola's research developed from a study of the alkylation of the iminazoles which he had prepared from 2 : 3 : 6-trinitro-*p*-acetamidophenol. These iminazoles could be methylated with methyl iodide on the 3-nitrogen to give methiodides which by aqueous acids were converted into ammonium hydroxides (I) and by alkalis into the isomeric carbinols (II), thus:



(I.) (II.) (III.)

The ammonium base readily lost water to give a compound of type (III) which Meldola called a "quinoneimide" although he adduced arguments in favour of a betaine structure, since the quinoneimide structure involved five carbon-to-nitrogen bonds for a nitrogen atom. The stability of these iminazole derivatives was noteworthy since O. Fischer's work had shown that known iminazoles alkylated on the 3-nitrogen atom were readily hydrolysed to diamines by alkaline reagents by fission of the heterocyclic ring. Meldola found the tendency to form the "quinoneimide" so strong that prior methylation of the hydroxyl group did not prevent it, methyl alcohol being eliminated (Meldola and Kuntzen, *J.*, 1911, **99**, 1283, 2034).

Meldola had noted the relationship of his "quinoneimides" to the ammonium bases prepared many years earlier by Griess by alkylating *o*- and *p*-aminophenol, and represented by him by the formula $C_6H_4<{}^{O}_{N(CH_3)_3}$ (*Ber.*, 1880, **13**, 246, 647). Meldola therefore commenced a study of *iso*picramic acid (2 : 6-dinitro-*p*-aminophenol) and prepared from that a corresponding trimethylammonium anhydro-base. The nitro-groups in this base were successively reduced and diazotised and the diazo-group replaced by halogen. In this way a dibrominated compound was obtained identical with that prepared by brominating Griess's base. Meldola had the ambition to prepare a base of this character containing three different radicals attached to the nitrogen atom and to resolve such a compound into components having optical activity due to an asymmetric nitrogen atom. There were experimental difficulties, however, due to the fact that, in the last stage of alkylation of the aminophenol, groups heavier than methyl alkylated the hydroxyl group instead of forming a quaternary ammonium compound, and the project was never achieved (Meldola and Hollely, *J.*, 1912, **101**, 912; 1913, **103**, 177; 1914, **105**, 977, 1469, 2073). The papers in which this work is described are characterised by a wealth of detail, including many observations and comments on the colours of the nitroaminophenols and compounds derived from them, and of their salts with acids and bases. A start was made on the study of the absorption spectrum of some of these compounds in collaboration with J. T. Hewitt (*J.*, 1913, **103**, 876) and would no doubt have been pursued had Meldola's life been prolonged. It was fitting that his fundamental interest in colour, awakened at the beginning of his career, persisted to the end.

HAROLD BAILY DIXON

1852—1930

HAROLD BAILY DIXON, whose work on gaseous explosions opened a new era in combustion research, was born in London on August 11th, 1852, the second son of William Hepworth Dixon (1821—1879), traveller and historical writer, who for some years was editor of the *Athenæum*. Although the family came of an old Lancashire Puritan stock, the Dixons of Heaton Royds, the grandfather of the chemist was Abner Dixon of Holmfirth and Kirkburton in the West Riding of Yorkshire, and his grandmother was Mary Cryer of those parts.

His father, William Hepworth Dixon, who was born in 1821 at Great Ancoats in Manchester, began life as a clerk in that city; but early resolving to adopt literature as a career, he became associated with a group of literary men, including Harrison Ainsworth, who were working in Manchester in early Victorian days. In 1846, at the instance of his friend Douglas Jerrold, he migrated to London; and, having early married a lively, good-looking, Irish girl, Marion MacMahon, they had eight children, of whom Harold Bailey (second son) and Ella Hepworth (youngest daughter) achieved distinction in science and literature respectively.

William Hepworth Dixon travelled extensively and wrote many popular historical books in a lively and attractive style. His house in Regent's Park was resorted to by a brilliant group of friends, among whom were Richard Burton, Bulwer Lytton, Frederick Leighton, John E. Millais, Thomas Firth, T. H. Huxley, Henry Irving, J. L. Toole, as well as J. M. Levy, founder and editor of the *Daily Telegraph*, and a certain tall, good-looking sapper called Kitchener. It has been said that, " although occasionally deficient in tact, Hepworth Dixon was faultless in temper and seldom put out by any disappointment or misfortune ". His sympathies were with the people, and he took a leading part in establishing the Shaftesbury Park and other centres of improved dwellings for the labouring classes. As a member of the first London School Board

[Reproduced by permission of the Royal Society.

Harold B. Dixon

(1870—73) he carried a resolution, in the teeth of strong opposition, establishing physical drill in all rate-paid schools throughout the metropolis; and in 1874 he persuaded the then Prime Minister (Disraeli) to order the opening of the Tower of London to the public free of charge. Besides good looks and physical build, Harold inherited from his father the exceedingly equable temper, liberal views, and strong current of sympathy for working people and their material and intellectual welfare which characterised his future life-work at Manchester University among the men of Lancashire and Yorkshire.

His mother was a woman of innate good taste and manners, with advanced views on the subject of women's suffrage; she went by herself to all Ibsen's plays, when they were first produced in London, and called in a lady doctor when her youngest son was born. Except, perhaps, for a certain liveliness on occasions of unusual excitement, when he would let himself go, it would be difficult to trace what influence her Irish blood may have imparted to her son Harold, who outwardly showed little sign of it, and was singularly reticent about his parents and early home-life.

In 1867 Harold was elected foundation scholar at Westminster School, from which in 1870 he obtained a classical junior studentship at Christ Church, Oxford. As an undergraduate he was one of the most popular men of his time, and threw himself into the social and athletic side of university life. He rowed in the College eight, played cricket, and took part in the last game of Association football in which a University team won the English Cup. He was also extremely fond of dancing. These activities so much interfered with his classical studies that he scarcely fulfilled the expectations of his tutors and there was a danger of his University career being brought to an untimely end. Fortunately, however, in 1873 Dr. A. Vernon Harcourt induced the College authorities to transfer the young classical scholar to his care, and was thus responsible for saving for chemical science one who was destined to be numbered among its most original and lucid exponents.

Two years later Dixon graduated first-class in the Natural Science School, and was elected to a fellowship at Trinity. He then started research work with Harcourt, who, some eight years previously in conjunction with Esson, had published his classical work on the rate of chemical change between solutions of hydrogen peroxide and hydriodic acid, which may be said to have founded modern

chemical dynamics. Until 1879, Dixon and Harcourt worked side by side in the crypt of one of the monastic buildings on the site of which Christ Church was built. It was the room in which the first anatomical studies were carried on, chiefly upon the bodies of malefactors who had been executed within the precincts of the Castle near by. Also it was in this room that, in the seventeenth century, the fortunate (or unfortunate) Mary Baker was revived by the surgeons after she had been hanged for an hour. Despite such gruesome associations, however, it made an admirable chemical research laboratory, being very quiet, of even temperature, and comparatively free from dust.

In 1879, Balliol and Trinity College combined in a joint scheme for the teaching of science whereby Trinity established the Millard Lectureship, to which Dixon was forthwith appointed, and Balliol provided a laboratory and lecture-room. A doorway, dubbed the "scientific frontier", was opened between the two Colleges so that Trinity men might have easy access to the new rooms. Dixon then transferred his research work to a cellar in the garden quadrangle which had been used by Benjamin Brodie for his investigations on ozone. It was damp and dark, and being devoid of any draught chamber, fumes used to rise up the staircase to the annoyance of the undergraduates having rooms above, who on one occasion were provoked to reprisals. One day, also, Dixon was so badly gassed by an accidental escape of carbonic oxide that, to the alarm of his assistant, he was in a state of complete aphasia for the next four hours. And on a third occasion it was only his presence of mind in turning off the tap of a gas-holder containing 30 cubic feet of an explosive mixture that prevented its being exploded by a flame originated by a premature spark in an apparatus which was being filled with it at the time. In 1886 he was elected to a fellowship at Balliol, and continued working there until he removed to Manchester in 1887, being assisted for some time (1883—85) by H. B. Baker.

It was at the instigation of Vernon Harcourt that Dixon commenced studying gaseous explosions in 1876; although, curiously enough, two years previously (October 2nd, 1874) his father's house in Regent's Park, London, had been completely wrecked by concussion waves from an explosion of gunpowder on the Regent's Canal near by.

During the sixty years which had elapsed since Humphry Davy's pioneering work on the subject, only R. W. Bunsen amongst

chemists had much explored it; and for twenty years his results had been accepted without question as authoritative. More particularly the results of Bunsen's experiments (1853) on the explosion of mixtures of electrolytic gas with increasing amounts of carbonic oxide were held to be *inconsistent* with the *principle of* "mass action" enunciated by Berthollet in 1805, and led to the curious view that a continuous alteration in the composition of such a gaseous medium produces a discontinuous ("*per saltum*") alteration in the course and products of its explosion.

In the year 1877, during the course of a research primarily undertaken to test Bunsen's conclusion, Dixon made his epoch-making discovery that the prolonged drying over phosphoric anhydride of a mixture of carbonic oxide and oxygen in combining proportions renders it non-explosive when subjected to electric sparks of an intensity sufficient to ignite readily an undried medium. He first announced it in a paper to Section B of the British Association at Swansea on August 28th, 1880 (*B.A. Reports*, 1880, p. 503), on which occasion he demonstrated it experimentally, adding that although the smallest addition of steam, hydrogen, or other vapour to the phosphoric anhydride-dried $2CO + O_2$ medium rendered it explosive, neither dry nitrogen nor dry carbonic acid nor dry cyanogen had any effect, from which "it appears probable that the oxidation of carbonic oxide is really caused by the alternate reduction and oxidation of water molecules, according to the equation:

(i) $CO + H_2O = CO_2 + H_2$

(ii) $2H_2 + O_2 = 2H_2O$".

Subsequently Dixon proved that the speed of flame in a $2CO + O_2$ explosion, whether during the initial phase of uniform slow movement or even after "detonation" had been set up, increases with the moisture content of the medium, up to "saturation" at about 35° when about 5·6 per cent. of it is present, a result which has since been confirmed by other investigators.

This discovery aroused world-wide interest and opened up a new field of chemical investigation which attracted workers from all quarters. As Dixon said, "it loosed a hare which, though since pursued by the hounds in full cry, is still uncaptured".

For many years much controversy raged round various chemical theories (including the one originally favoured by Dixon) which from time to time were put forward to explain the comparative inertness of dry carbonic oxide–oxygen media, and many important

experiments were made in attempts to discriminate between them. M. Traube and Lothar Meyer in Germany, Beketoff and Mendeléeff in Russia, H. E. Armstrong, as well as Dixon and his pupils in this country, figured prominently in the discussions. Nowadays, while not rejecting the well-known chemical interactions of both steam and hydrogen peroxide with carbonic oxide as partial explanations (especially when massive proportions of such "promoters" are present), there is a growing consensus of opinion favouring a physical explanation of the phenomenon, which latterly Dixon himself more and more inclined to. Indeed, his last published words upon the subject (in reviewing some experiments on the influence of a strong electric field on the combustion of a rigidly dried $2CO + O_2$ medium) were that "it was evident that the resistance to combination offered by the dryness of the gases could be overcome by the electrostatic field . . . (so) that the problem presented by the burning of this gas has become one of the most interesting in physical chemistry".*

Dixon's early Oxford researches (1876—81), besides proving, *contra* Bunsen, the validity of Berthollet's "law of mass action"—a conclusion which was simultaneously established by the independent work of Horstmann in Heidelberg—laid a firm and lasting foundation upon which much later work on equilibria in reversible gaseous interactions has been built.

Until the year 1880, on the strength of some measurements made by R. W. Bunsen in 1857, it was generally believed that gaseous explosions travel at rates not exceeding a few metres per second only; but on July 5th of that year a disastrous explosion in a 36-inch gas-main in Percy and Charlotte Streets and Fitzroy Square near Tottenham Court Road, London, involving the loss of two lives and much damage to property in the neighbourhood, afforded conclusive evidence of much higher speeds. Vernon Harcourt, who had been called in to investigate the matter, suggested to Dixon the desirability of his undertaking a systematic investigation of the rates of propagation of flames in gaseous explosions generally, which he forthwith began. He had not got far with it, however, before Berthelot and Vieille announced (1880) their discovery of the high constant flame speeds finally attained on the development of "l'onde explosive" ("detonation") in gaseous explosions. This

* *Nature*, 1929, **129**, 582. Also, a complete review of fifty years' work (1880—1930) on the subject is given in the Third Liversidge Lecture before the Chemical Society by W. A. Bone (*J.* 1931, 338).

revelation, together with the appearance of Mallard and Le Chatelier's classical *Recherches expérimentales et théoriques sur la combustion des mélanges gaseux explosifs*, in 1883, showed that the comparatively slow flame speeds observed and measured by Bunsen apply only to the mild and usually short initial phase of such explosions.

Working on parallel lines with these French savants during the next twenty years, Dixon so successfully developed the methods initiated by them that he soon became a leading authority on the subject. In 1893 he gave the Bakerian Lecture on "The Rates of Explosion in Gases", and nine years later published in the *Philosophical Transactions* of the Royal Society a brilliant memoir embodying his photographic researches on "The Movements of Flame in the Explosion of Gases".

The method adopted by Dixon for measuring "rates of explosion" ("detonation") in gaseous explosions followed closely in principle that originated by Berthelot and Vieille; but his determinations were more systematic and in some cases more accurate than theirs. They concluded that the velocity of the "explosion wave" is quite independent of the material and diameter of the tube employed, provided that a certain small limiting diameter is exceeded, as well as independent of the pressure; the last-named conclusion, however, Dixon subsequently found erroneous by showing that the rate increases slightly with pressure, at least up to two atmospheres. Berthelot and Vieille termed it, for a given explosive mixture, "*une propriété fondamentale ; car elle établit que la vitesse de propagation de l'onde explosive est réglée par les mêmes lois générales que la vitesse du son*"; and, assuming that it equals, or approximates closely to, the mean velocity of translation of the molecules at the moment of combination, supposing them to retain all the heat developed in the reaction, they found agreement with the theoretical rate calculated by the formula of Clausius

$$v = 29{\cdot}354 \sqrt{T/d},$$

where T = the maximum temperature (abs.) reached in the explosion, and d = density of the products of combustion referred to air.

Berthelot and Vieille further assumed (i) $T = Q/6{\cdot}8n$, where Q = the heat liberated by the chemical change involved in the propagation of the wave, and n = the number of "molecular volumes" taking part therein; also (ii) that the gases are heated at *constant*

pressure, (iii) that the specific heat of a compound gas is the sum of the specific heats of its constituents, and (iv) that " dissociation " scarcely affects the propagation of the wave, because of its extremely short duration and the high pressures developed therein. Although it so happened that the velocity (2810 metres per second) which they actually found for electrolytic gas ($2H_2 + O_2$) came very near the 2831 metres per second calculated on the foregoing assumptions, most of their other observed experimental values fell short of the calculated values, and notably the observed 1089 as compared with the calculated 1941 metres per second in the case of a $2CO + O_2$ medium. This led them to regard their formula as " provisional " only, in the same sense that it gave a *limit* representing the *maximum* possible rate of propagation and subject to diminution in various ways, combustion, as they said, in many cases " *se propageant alors de proche en proche suivant une loi beaucoup plus lente* ".

While adopting the " sound-wave " theory of Berthelot and Vieille in principle, Dixon subjected it in his Bakerian Lecture to a searching criticism in detail, more particularly in regard to certain assumptions, with which he disagreed. He sought to modify it so as to make it better fit the facts by supposing that (i) the explosion wave is carried forward by movements of molecules of density intermediate between that of the products of combustion and that of the unburnt gases, (ii) the gases are heated at constant volume (not constant pressure), (iii) the temperature of the gas propagating the wave is double that due to the chemical reaction alone, and (iv) the velocity of a sound wave is only 0·7 of the mean velocity of the molecules in the medium through which it is passing.

Even when so modified, however, the " sound-wave " theory predicted in a number of cases (*e.g.*, most undiluted detonating mixtures) rates of explosion so much higher than those actually observed—*e.g.*, for undiluted electrolytic gas the " calculated " rate was 3416 as compared with the found value of 2830 metres per second—that eventually it had to be abandoned. Indeed, both its French authors and Dixon had quite erroneously assumed the heat capacities of gases to be independent of temperature, while Dixon over-estimated what he thought to be the limiting influence of " dissociation " in the wave. In 1910, he confessed quite frankly, " I do not believe to-day in the truth of my working hypothesis of the explosion wave. It embodied a number of assumptions, some of which I have myself shown to be erroneous. The theory of the explosion wave is not to-day dependent on the

hypothesis of Berthelot and myself." And at the same time he expressed his conversion to the newer views advanced independently by Hugoniot (1887—88), D. L. Chapman (1899), Vieille (1899—1900), and E. Jouguet (1906), according to which "detonation" is essentially a "shock wave" propagated through a medium which is discontinuous in the vicinity of the wave front, in the sense that an abrupt change in pressure and density in the vicinity of the wave front is propagated and maintained from layer to layer by the adiabatic ignition of the explosive medium, a conception which has now superseded the former "sound-wave" theory.

The great and permanent value of Dixon's work in this connection really lay both in his accurate and systematic measurements of "rates of explosion" ("detonation"), most of which were set forth in his Bakerian Lecture (*q.v.*), and in certain important conclusions which he deduced therefrom regarding the chemical reactions actually concerned in the propagation of the wave. Thus, for example:

(i) His observed rates for the following cyanogen mixtures:

$$\frac{C_2N_2 + O_2}{2728} \left\{ \begin{array}{cc} \dfrac{C_2N_2 + 2O_2}{2321} & \dfrac{C_2N_2 + 3O_2}{2110} \\ \dfrac{C_2N_2 + O_2 + N_2}{2398} & \dfrac{C_2N_2 + O_2 + 2N_2}{2166} \end{array} \right\} \text{metres per second}$$

showed that the gas burns in two well-defined stages, namely (*a*) primarily to carbonic oxide in the wave itself, and (*b*) afterwards to carbon dioxide behind it.

(ii) His observed rates (at 10° and 760 mm.) for the following hydrocarbons with varying proportions of oxygen showed that (*a*) there are distinct stages in the explosive combustion of a hydrocarbon, and (*b*) *in the wave itself* the carbon burns primarily to carbonic oxide, which afterwards burns to carbon dioxide in the rear of the wave, the rate of explosion for a mixture containing sufficient oxygen for *complete* combustion being always much less than that for one containing only sufficient oxygen to burn the carbon to carbonic oxide; thus he found:

Methane–Oxygen Mixtures.

$$\frac{CH_4 + O_2}{2528} \qquad \frac{CH_4 + 1\frac{1}{2}O_2}{2470} \qquad \frac{CH_4 + 2O_2}{2322} \text{ metres per second.}$$

Ethylene–Oxygen Mixtures.

$\dfrac{C_2H_4 + O_2}{2507}$ $\dfrac{C_2H_4 + 2O_2}{2581}$ $\dfrac{C_2H_4 + 3O_2}{2368}$ metres per second.

Acetylene–Oxygen Mixtures.

$\dfrac{C_2H_2 + O_2}{2961}$ $\dfrac{C_2H_2 + 1\frac{1}{2}O_2}{2716}$ $\dfrac{C_2H_2 + 2\frac{1}{2}O_2}{2391}$ metres per second.

It was in connection with his foregoing determinations of the rates of explosion of hydrocarbons, which were mostly made in Manchester during 1891—92, that Dixon and his collaborators rediscovered the extremely important fact, first observed by Dalton in 1803—04 but afterwards long forgotten, that on explosion an equimolecular mixture of ethylene and oxygen yields about twice its own volume of carbon monoxide and hydrogen, in accordance with the equation

$$C_2H_4 + O_2 = 2CO + 2H_2.$$

This rediscovery, reinforced by similar observations by Smithells and Ingle (1892) on the interconal gases of aërated hydrocarbon flames, and by the experiments of W. A. Bone in conjunction with B. Lean and J. C. Cain on explosion of ethylene or acetylene with less than their own volumes of oxygen, finally laid the dogma of the preferential burning of hydrogen in hydrocarbon flames, which had been unquestioningly accepted among chemists as an article of faith for sixty years previously, thus clearing the ground for modern views of the mechanism of hydrocarbon combustion.

In 1886, while in the middle of his work on " rates of explosion ", Dixon was appointed to succeed Sir Henry Roscoe in the Chair of Chemistry at Owens College, Manchester; and this he occupied until his retirement in 1922, when he became honorary professor at the University, while continuing his researches right up to the day of his death. And it was in Manchester that his powers and life-work came to fullest fruition and that his greatest influence was exerted.

Under Roscoe and Schorlemmer the Manchester School of Chemistry had become so famous and dominant in the country that many predicted its reputation would inevitably suffer through the former's supersession by a comparatively young and untried Oxford don. But Dixon's outstanding administrative gifts, his devotion to experimental research, his brilliance as a lecturer, his power of arousing in his students the true spirit of enquiry, and the way in

which he always identified himself with the social and athletic sides of the College and University, proved more than equal to the task, so that the reputation of the School continually increased under his leadership. He was indeed the *beau idéal* of a university professor.

When Dixon went to Owens College in 1887, its professoriate included Horace Lamb (Mathematics), Balfour Stewart and A. Schuster (Physics), Osborne Reynolds (Engineering), Carl Schorlemmer (Organic Chemistry), W. C. Williamson (Botany), Milnes Marshall (Zoology), Boyd Dawkins (Geology), Robert Adamson (Philosophy), A. W. Ward (History), A. W. Wilkins (Latin), and Alfred Hopkinson (Law). His own chemical staff comprised Carl Schorlemmer, G. H. Bailey, Harry Baker, J. B. Cohen, and Watson Smith; and a year later G. J. Fowler and A. Harden joined it. It was probably at the time the strongest chemical teaching staff in the country, and the splendid lecture theatre and laboratories which had been built fifteen years previously under Roscoe's supervision were unsurpassed in those days.

It did not take Dixon long to settle down and get to work in such a congenial environment, which powerfully stimulated and developed his scientific and administrative powers; and he soon attracted round him a band of enthusiastic students and workers, with whose co-operation he founded his Manchester School of Combustion Research. His first research assistants were H. W. Smith and G. H. Turpin (1888), followed by W. A. Bone and B. Lean (1891), E. H. Strange and E. Graham (1894), E. J. Russell (1896), and, later, R. H. Jones and L. Bower, all of whom collaborated with him in the experimental work on gaseous explosions during the period 1888—1903, the results of which were ultimately embodied in two *magna opera* in the *Philosophical Transactions* of the Royal Society in 1892 and 1903, as well as in other papers published in the *Journal of the Chemical Society* between those years.

Before dealing with Dixon's researches at Manchester, something should be said about his direction and development of its great chemical school. In some respects his start off was not altogether auspicious. Under his predecessor, Roscoe, who for some years (1852—56) before his appointment to Manchester in 1857 had been closely associated in research with Bunsen in Heidelberg, the school had been steeped in Bunsen traditions, and naturally enough at first some of the old hands did not take very kindly to the succession of an Oxford don who not only plumed himself on having upset Bunsen's conclusions about gaseous explosions, but also had

quite other ideas about teaching, and left the supervision of routine laboratory work mainly to his subordinates. This feeling, however, soon died down when they discovered how keen Dixon was on giving everyone ample opportunities for research, and how great were his gifts as a leader and an administrator. And henceforth he was strongly supported by all concerned, and success was both great and unbroken.

In 1892 his colleague Schorlemmer died and was succeeded by William H. Perkin, jun., whose dynamic personality and unrivalled technique infused such new vigour into the organic side of the school that soon its laboratories so overflowed with students and researchers that extension of its buildings and equipment became necessary. The successive addition of the "Schorlemmer", "Schunck", and "Morley" laboratories barely sufficed to accommodate the ever-increasing crowd of workers. Work went on busily day and night during term-time and vacation, throughout the whole year in never-ceasing activity. The fame of it spread into many lands and "fired the heather" throughout the North. The youth of Lancashire and Yorkshire "caught on" and joined up in their scores. There is a spirit in the bleak Northern moorlands—

"*where th'east wind blows snell an' keen*"

—that knows great leadership and "scents battle from afar", and in the 'nineties Dixon and Perkin captured it for chemical science. Although differing widely in temperament, upbringing, and outlook, they shared a common enthusiasm for experimental research, gave each other constant and ungrudging mutual support, and proved an ideal combination for the development of a great chemical school. In 1913 they were joined in the Manchester professoriate by A. Lapworth, who eventually succeeded Dixon on his retirement in 1922. Of their lieutenants and pupils, W. A. Bone, H. C. H. Carpenter, D. L. Chapman, J. B. Cohen, A. W. Crossley, A. Harden, W. N. Haworth, J. W. Mellor, F. L. Pyman, Robert Robinson, E. J. Russell, and J. F. Thorpe subsequently became Fellows of the Royal Society; P. J. Hartog, B. Lean, Norman Smith, and G. S. Turpin achieved distinction in educational affairs; while G. W. Andrew, G. H. Bailey, E. Bury, H. G. Colman, T. Ewan, G. F. Fowler, H. Hartley, D. S. Jerdan, H. Levinstein, R. Lessing, G. P. Pollitt, R. E. Slade, and R. V. Wheeler, to mention a few only out of many, subsequently made their mark in industry and technology.

After completion of the work on rates of explosion in the early 'nineties, Dixon's researches (though comprising also the combustion of both carbon and carbon disulphide, as well as further experiments on the influence of moisture in the combustion of carbonic oxide) were chiefly photographic studies of flame movements in explosions. In this work Dixon had the collaboration first of E. H. Strange and E. Graham, and afterwards of R. H. Jones and L. Bower. Although the method adopted—namely, that of photographing a horizontally moving flame on a film moving vertically with known velocity—was in principle the same as had been originated by Mallard and Le Chatelier in 1880—83, it was so vastly improved and developed in detail as to become a very refined and accurate method of flame analysis. It was first described in a paper "On the Explosion of Cyanogen" communicated to the Chemical Society in 1903; but the memoir embodying the full results obtained appeared in *Philosophical Transactions* for 1903. Meanwhile both Berthelot and Le Chatelier, who had been working on similar lines in France, published papers on the subject in 1899 and 1900.

It is impossible in the short space at our disposal to give any adequate idea of the wealth of information contained in the seventy or more photographs of explosion flames included in Dixon's 1903 memoir; and the only way for anyone to understand their value is to study them closely in detail. Suffice it to say that the whole course of a gaseous explosion, from its initial phase of slow uniform flame movement up to its culmination in detonation, was photographically analysed with great precision. Not only were the influences of compression waves and the collision of detonation waves illustrated, but discoveries were made of (i) the backward "retonation wave" which is always set up when detonation is determined in a gaseous explosive medium, and (ii) the "reflection waves" which arise when a detonation wave is either arrested by the closed end of a tube or momentarily retarded on passing a constriction in it. Similar discoveries were simultaneously made independently by Le Chatelier in France, so that the years 1900—03 saw a remarkable resuscitation of the interest aroused twenty years previously by the kindred researches of the same masters.

Dixon's third principal line of research which chiefly occupied him after 1903, and in which he was assisted by H. F. Coward, J. M. Crofts, L. Bradshaw, C. Campbell, and others, was concerned with the "ignition temperatures" of explosive gaseous media, which

he was the first to determine with any real degree of accuracy. Previous attempts, notably by V. Meyer and pupils in Germany, and Emich in Austria, had been frustrated by the considerable amount of pre-flame surface-combustion which always had occurred in their experiments before the explosive medium as a whole had been raised to the true ignition point. To obviate this source of error, Dixon and Coward devised their well-known "concentric-tube" method, in which streams of combustible gas and air (or oxygen) were separately heated to the temperature of the medium before being allowed to mix. In this way the "ignition range" at atmospheric pressure of hydrogen was found to be 580—590° in both air and oxygen, of moist carbonic oxide 644—658° in air and 637—658° in oxygen, of acetylene 406—440° in air and 416—444° in oxygen, and so on. Paraffin hydrocarbons, such as methane and ethane, were similarly found to have much wider "ignition ranges", *e.g.*, that of methane was 650—750° in air and 556—700° in oxygen. Later on, after it was discovered that the earlier results had been affected by the fact that when an explosive mixture is rapidly heated even to its "ignition point" an appreciable "lag" may occur *in the actual appearance of flame*, the concentric-tube apparatus and procedure were modified so as to control and determine such "lag". In this way it was found that the longer the "lag" allowed, the lower the resulting ignition temperature. Thus, for example, in the case of hydrogen at atmospheric pressure for a "lag" of 0·5 second only, the "ignition emperature" was 631° in air and 625° in oxygen, but on allowing a "lag" of 10 seconds temperatures of 588° and 582° only were required.

In 1906—07 H. G. Falk, acting on a suggestion by W. Nernst, had endeavoured to determine the ignition temperatures of various *gaseous explosive mixtures under adiabatic compression*, by compressing them in a steel cylinder the piston of which was suddenly driven in by means of a falling weight; and, finding that with hydrogen-oxygen mixtures the equimolecular mixture required the least degree of compression (corresponding with a temperature of 518°) for its ignition, he concluded that hydrogen peroxide, and not steam, is the first product of the reaction.

Dixon, who never believed in any "peroxide" theory of combustion, at once took up the matter in conjunction with J. M. Crofts, and had no difficulty in proving not only that Falk's experimental method had been faulty in that the piston had not been stopped at the beginning of the pre-flame period, but also that two of his

assumptions were generally invalid. On publishing their own experiments in 1914, they had no difficulty in showing that his conclusion regarding the ignition of hydrogen–oxygen mixtures was entirely wrong. They showed that (i) the true ignition temperature of electrolytic gas under adiabatic compression is 526°, and (ii) whereas successive dilutions of it with either hydrogen or nitrogen continually raise, dilutions with oxygen continually depress, the ignition temperature, such depressions continuing long after the $H_2 + O_2$ ratio has been passed. At the time this unexpected result suggested to them the formation of some active " polymeride " of oxygen under the experimental conditions; but nowadays it would not be regarded as indicating more than some prior " activation " of oxygen as a condition precedent to the combustion.

Dixon continued his work on ignition phenomena right up to the end, and further discovered (*inter alia*) that " ignition temperatures " of a gaseous medium are, or may be, profoundly affected by the presence of small amounts of impurities therein. Thus he found, for example, that whereas the presence of small quantities of oxides of nitrogen lowers, that of iodine vapour materially raises, the ignition temperature. It was, in fact, on experiments arising out of the action of iodine that Dixon was engaged in his laboratory a few hours only before his sudden death at Lytham in the afternoon of September 18th, 1930, thus leaving an " unfinished symphony " for his pupils to complete.

Although Dixon devoted his scientific life to the study of combustion, other problems in inorganic chemistry sometimes occupied his attention. Among them the one which showed a notable advance on any preceding work on the subject was his determination, with E. C. Edgar, of the atomic weight of chlorine (*Phil. Trans.*, 1905, 169). A few years previously, Edward Morley had determined, with an accuracy never before approached, the direct ratio of the combination of hydrogen with oxygen. Since very many atomic weights depend on the synthesis or analysis of oxides, Morley's result led to the correction of a large number of these constants. But in 1905 the atomic weights which depended on the analysis of chlorides were also numerous, and the determination of the ratio of hydrogen to chlorine was therefore important. The weighing of chlorine was the great difficulty. It was solved by liquefying the gas in a weighed bulb and weighing it at the ordinary temperature. Since no ordinary glass tap would stand the pressure, the plug always blowing out, Dixon had taps made in which the slope of the plug was

reversed, so that the greater the pressure, the tighter was the tap. This ingenious modification enabled a most concordant series of values to be obtained, and the atomic weight of chlorine determined by Dixon and Edgar is in agreement with that at present accepted.

Besides being both a great exponent of the experimental method in science and an able administrator, Dixon shone brilliantly as a lecturer, teacher, and master trainer of those who were privileged to be his pupils in research; and it was as such that the influence of his personality was most markedly felt. He prided himself most on having founded an English School of Combustion Research embodying the traditions of Robert Boyle and Humphry Davy, with whom he ranks in apostolic succession. In writing on August 26th, 1927, about the publication of "Flame and Combustion in Gases", which had been dedicated to him he said, "I think you know that I regard the chief reward of my work to lie in the fact that when I started fifty years ago to repeat Bunsen's experiments, no one in England seemed to care about the burning of gases, and now there is an active English School largely made up of old students . . . really keen on the fundamental study of gas reactions." And it is worth while considering how this resulted from his work and influence.

First of all, his lectures, distinguished as they always were by great clearness, logical presentment, and wealth of experimental illustration, aimed chiefly at expounding principles, as exemplified by the researches of great masters, and at arousing in his students the true scientific spirit of enquiry. One of his most distinguished pupils has testified that "his account of the classical investigations showed how discoveries were made, the ideas at the back of the minds of the investigators, and the methods whereby they overcame difficulties. Personally, I found this method most inspiring, and far better than any exposition of the results. As he used it, the historic method was a splendid instrument for training research pupils, and it undoubtedly helped all his students." Indeed, no one privileged to hear his lectures could fail to be impressed by the acumen and power of a great teacher.

Next, he had an unusually sound critical faculty and complete mastery of clear exposition in the best and most concise of English. In his earlier days in Manchester, while yet his school was of such dimensions as allowed it, he would get his "first year honours" pupils to write him weekly essays on some subject arising out of his lectures, and in a special weekly tutorial he dealt with their

efforts, reading out and criticising passages from them. Each of his "third year" students was required, about twice each term, to write an exhaustive essay on some subject of the day, after reading and abstracting all the principal researches upon it; and it was Dixon's invariable custom to go privately through each composition with its author, sometimes spending hours even in criticising and discussing it. He never let any weakness in argument, inconsistency in statement, or loose expression go by uncorrected, and was untiring in his efforts to evoke good literary style and habits. Not only so, but on occasion he would ask a senior research assistant to lecture to him on the subject of an essay, in order to train him in oral exposition. Many of his pupils owed a great deal to him in these respects.

Lastly, his singularly clear and penetrative mind referred everything to the final test of a well-ordered experiment, critically carried out without hurry or bias, and with the results checked at every conceivable point. He insisted on everything being done with the greatest care and circumspection, and afterwards subjected to the most rigorous examination. At all times he was unsparing in the guidance of his experience and unrelaxing in impressing on all concerned the paramount importance of accuracy and truth, together with the highest standard of experimental work. He always held that what apparently are the simplest cases of chemical change are fundamentally the most obscure and worth while investigating. His method was first of all to get at the facts with all due precautions against possible errors, then to consider critically their bearing on the matter involved, and to advance the experimental proof step by step, by a process of exclusion, until it had been narrowed down to a single issue which finally had to be tested in every possible way. And, at the end of it all, he would often constitute himself the *advocatus diaboli*, trying his hardest to upset the verdict. Not long before his death he remarked that he had never seen any law or theory relating to flame and combustion which could not either be disproved or shown inadequate, so varied and complex are the possibilities, adding, "I know no law of flame, nor want to". By eschewing all rash speculation and attaching little importance to theories save as working hypotheses, Dixon allowed the clear light of science to shine through all his work, and he had a singular felicity in choosing just the right words in expounding it. Being associated with him in research meant, not only having to excel as a craftsman, but undergoing a most

exacting mental discipline, which only strong minds could stand; but to them it became the way of understanding.

He always endeavoured to transfer to his teaching staff those of his research pupils and assistants whom he thought most highly of, and to retain them there for some years. Their pay was poor, and he did nothing to improve it, regarding it as part of a salutary discipline; but in compensation he arranged the duties so that each one had half his time for research, and was given all possible facilities for pursuing it independently. And he was against anyone accepting a better post outside until research had become his ingrained habit and he had established some reputation as an independent worker. Hard and long as was the discipline, everyone who underwent it was conscious of being handled with real appreciation and understanding, however austerely, and ever afterwards was thankful for it.

From Manchester many of his pupils went forth to plant research colonies in other centres, and in later years he took great delight in visiting them. So keen was his interest that he would journey any distance to see a new experiment, or correspond at any length about it. In visiting his pupils' laboratories he would watch everything with a most critical eye, quick to take in every point of an experiment, and to detect the slightest flicker of a flame; but when he had convinced himself of the genuineness of a new result, his appreciation of it was both deep and sincere. At times, on such occasions, he would sit up to well-nigh daybreak discussing the results and comparing them with his own; and always he gave generously of his experience, whether personally or by letter.

Although Dixon always took an active share (as member of its Court and Council) in Manchester University affairs, and managed his own Department of it supremely well, it would not be easy to point to anything which he specifically influenced except the social and athletic sides of student life, in which he always took the greatest interest, and the work of the Joint Matriculation Board of the Northern Universities, of which he was Treasurer for fifteen years. He was prominent among those who organised the Faculty of Science in the newly constituted University in 1903, after the break up of the old federal Victoria University and the granting of separate charters to Manchester, Liverpool, and Leeds. It was mainly through his energy that the present splendid University athletic ground and pavilion at Fallowfield were secured.

Outside the University, Dixon played a notable part in the

educational affairs of Manchester and Salford. He took a great interest in the Manchester High School for Girls, and in the Pendleton High School, both of which owe a tremendous debt to him. Also, for many years he was co-opted member of the Salford Education Committee, and Chairman of its Higher Education Committee, as well as of its Royal Technical College and its three secondary schools; all these positions he continued to fill until the end with conspicuous success and great advantage to the public. Latterly he devoted much time to the establishment of the new Queen Mary's Secondary School for girls at Lytham, and was returning from a meeting in this connection at Lytham when he was suddenly taken ill and died.

Dixon was elected Fellow of the Royal Society in 1886, was the Bakerian Lecturer in 1893, served on its Council during 1902—04, and was awarded one of its Royal Medals in 1913. In 1922 the University of Manchester conferred upon him its D.Sc. *honoris causa*, the University of Prague having similarly conferred its Ph.D. some years previously. In view of the outstanding importance of his scientific work it may seem strange that these were the only honorary academic distinctions conferred upon him; but Dixon was markedly indifferent about such honours, and never sought after them.

Dixon joined the Chemical Society in 1876, and contributed his first paper to the *Journal* in 1885. He was elected to the Council in 1892, and served thereon for a period of twenty-five years in all, occupying the office of President from 1909 to 1911.

He presided over the Chemical Section of the British Association at its Oxford Meeting in 1894, when he delivered a memorable address entitled "An Oxford School of Chemists", in which he charmingly reviewed the work of Robert Boyle and his pupils, Robert Hooke and John Mayow. He was President of the Manchester Literary and Philosophical Society during 1907—09 and 1923—25. He was always ready to serve the public interest. In 1881 he made experiments for the Board of Trade on standards of light to be used in photometry, and three years later he made photometric measurements on various illuminants at the experimental lighthouses erected by Trinity House on the South Foreland. He served on the Royal Commission on Explosions from Coal-dust in Mines (1891—94) and on Coal Supplies (1902—05); also he was a member of the Home Office Committee on Explosions in Mines (1911—14), and from 1927 carried out a series of researches on the

ignition of gases for the Safety of Mines Research Board. During the First World War he was Deputy Inspector of High Explosives for the Manchester area and Chairman of the Ministry of Labour Selective Committee for the North-Western District, for which services he was appointed C.B.E. in 1918.

Amid his manifold other interests, Dixon never lost his early love of the classics, and while voyaging to South Africa with the British Association in 1905 he produced for private circulation a verse translation of the Odes of Horace, which for scholarly treatment and real feeling could scarcely be surpassed. Indeed, Horace and Omar Khayyám were his favourite authors, and he was filled with the spirit of the "*Novum Organon*", of which his scientific work was the fruit.

As a boy, Harold Dixon was very handsome, his portrait being painted by Thomas Firth, R.A., and his head modelled by Bailey the sculptor, in both cases at the artist's request. Of medium height, with well-knit frame, throughout his life his was an arresting face and bearing in any social assembly. In outward features he bore a strikingly close resemblance to his great contemporary Berthelot, than whom he was twenty-five years younger. Indeed, at one time it was difficult to distinguish the two when they were together.

He was brilliant in conversation, and as an after-dinner speaker; a man of the world, he had much sympathy with the weakness of human nature, but was intolerant of all shams and bores. He had a remarkably equable temperament and *sang froid*, always showing great coolness and presence of mind in time of danger. A story is told how once during 1889 in Manchester when he and his assistant had miraculously escaped injury from the accidental explosion late one afternoon of the contents of a 10-cubic-foot holder full of electrolytic gas, which wrecked the room in which they were working, some three hours afterwards Dixon went out to a dinner-party, and on being asked by a lady whether he had heard of "that dreadful accident to a poor professor at Owens College", he replied, "Yes, I did hear a report!"

Although Dixon continued to play both cricket and tennis well into middle life, his chief physical recreation was mountaineering, in which he excelled. He climbed much with J. N. Collie and Milnes Marshall, being one of the party when the last-named lost his life on Scawfell on December 31st, 1893. During 1890—93 he accomplished more than twenty first-class climbs in the Alps,

and was elected to the Alpine Club in 1894. Afterwards, in 1897, he climbed in the Selkirks, Canada, making the first ascent of both Pollux and the Dome, and the second ascent of Castor, with C. E. Fay and others. Also, in the Canadian Rockies, he made the first ascents of Mounts Lefroy and Gordon with C. E. Fay, Norman Collie, and C. S. Thompson.

Although of a kindly disposition, and always most friendly towards his colleagues and assistants, being ever ready with practical sympathy and help in times of need and trouble (as many have testified), he was singularly reticent about himself and masked his real feelings. It was easy for a colleague or assistant to establish and continue friendly relations with him, but difficult to penetrate within his outer ring of electrons. The experience of one of his Manchester staff, who said, "I didn't feel after thirteen years' acquaintance that I knew him any better than after three months", would (we think) be shared by many others. Even to those of us who knew him longest and best it was rarely (if ever) that he revealed anything of his more intimate self. And while hosts of his old pupils will ever remember him with deep affection and gratitude, most of them will still wonder whether they ever really knew him at all.

He was twice married, first in 1885 to Olive Beechey Hopkins of Montreal, who died in 1917, and by whom he had a son and a daughter; and then in 1918 to Muriel Kinch of Yelverton (South Devon) who survived him, and by whom he had a daughter.

His mental powers were maintained quite unimpaired right up to the end, which came suddenly on September 18th, 1930. Only a few weeks before, when paying what proved to be his last visit to the laboratories of Professor Bone at the Imperial College, London, he spent most of the day seeing and discussing some new photographic experiments on the development of "detonation" in gaseous explosions. He examined the resulting flame photographs intently with all the old critical keenness of his practised eye. The hours sped by almost unnoticed; at last, suddenly looking at his watch, he exclaimed, brushing aside the photographs with a gesture of regret, "All these are most wonderful, my dear boy, but it is now past five o'clock and I must catch my train home, leaving them to you," and so departed. *Vale Magister Praeclare!*

WILLIAM RAMSAY

1852—1916

THE story of Ramsay's researches and discoveries has been told many times, and there is little to add to it without raising controversial issues, which should find no place here. But an opportunity offers, while some of those who worked under him as students, or served as members of his staff, are still here, to say something more about the man himself. All of his own generation have passed on, often leaving behind their correspondence with him, and there are the notes which they wrote for the late Sir William Tilden when he was writing "The Life of William Ramsay". That excellent memoir was written from the viewpoint of men of his own generation. We of a younger generation stand between his contemporaries and the historian, who will, at some later date, base the story of Ramsay's life and work on purely documentary evidence.

The career of a boy or girl of to-day is more or less fixed at the age of fifteen, when he passes the School Certificate Examination, and it is interesting to contrast the devious course by which Ramsay became a chemist. He was convinced that he had chemistry in his blood. His father's forbears had been dyers for generations, till his grandfather deviated slightly into manufacturing chemicals used in this industry. He was a man of ability, and corresponded with many distinguished chemists of his day. He founded the Chemical Society of Glasgow in 1800, and was its first President. He was credited with the discovery of bichromate of potassium, and of Turnbull's blue. Ramsay's father was trained as an engineer, and took part in the development of railways in Scotland; but early in his son's life he had taken up insurance business. Yet he retained an interest in science, and particularly in mathematics, and in geology, in which his brother, Sir Andrew Ramsay, attained eminence. Another brother, John, became a sugar-planter in Demerara, and founded a works equipped with up-to-date machines and with a laboratory in which investigations were carried on. He died early, leaving his library to his nephew. On his mother's side,

WILLIAM RAMSAY

Ramsay's forbears included more than one physician of distinction.

Whence came the genius shown by more than one member of the Ramsay family besides himself? That is a question we cannot answer. But the family tradition pointed in one direction, and Ramsay's close association with his father—for he was an only son and devoted to his parents—and with his uncle Andrew's family, had the result that he was brought up in a scientific atmosphere. Yet his mother's dearest wish was that he should enter the ministry, which accounts for the course which his education followed till he was sixteen years of age.

He was born in October, 1852, and in October, 1866, he matriculated at the University of Glasgow, and began to follow the University classes. The case was similar to that of a boy passing the School Certificate Examination, and then proceeding direct to the University, which cannot be done to-day, as the Universities do not provide junior classes. He followed an Arts course, reading classical languages, English, and later moral philosophy and logic, with but little mathematics. His course was undistinguished, but, as his friend Fyfe points out, he was by two years the junior in the class. However, he exhibited one of the qualities of genius—that of taking a great deal of trouble with his work. In June, 1868, he writes to his aunt, "I am writing out a logic lecture, which is about fifteen pages of quarto, I think. It takes me nearly three hours writing as hard as I can. They are not very interesting." He was not quite sixteen.

At sixteen-and-a-half he left the University. He was then at the standard reached by a sixth-form boy in a public school. But he had learned a great deal which was not included in the University course. Following the Bible-readings in church in French and German, and translating backwards and forwards, he had acquired a working knowledge of two foreign languages. He was to acquire a knowledge of several other languages later. He was interested in music, having a keen musical ear, and was a competent performer on the piano. He had also developed a unique accomplishment, whistling classical music to his own piano accompaniment. He was clever with his pencil, particularly at making sketch portraits of his friends, and he could write most amusing verses. He was not interested in ball games, though he played tennis occasionally, but as a swimmer he excelled, and few could equal him in under-water diving. He was certainly a good mixer, with an excellent

memory for names and faces, and he made not only a large circle of friends, but a host of acquaintances.

At the age of sixteen, so far as natural and acquired qualities were concerned, Ramsay was very well equipped to commence training for any future activities. He had had no training whatsoever in science, but he had been brought up in a scientific atmosphere, and he had made science somewhat of a hobby. He tells us that he first became interested in chemistry when, while recovering from a broken leg, he read Graham's "Chemistry". His father then gave him some small pieces of apparatus, and some chemicals. He seems to have avoided disaster by making friends with Fyfe, his class-fellow, who was attending Professor Anderson's lectures on chemistry in the University. Ramsay made his bedroom into a sort of laboratory, and there he and Fyfe experimented. What his mother thought about it was not recorded. However, during the years at the University he had no instruction in chemistry at all.

On leaving the University Ramsay entered the laboratory of Mr. R. R. Tatlock, the Glasgow City Analyst. This must have meant a breakaway from the training for the ministry, but one knows nothing about the circumstances of the change. He remained with Tatlock for eighteen months, or less. Tatlock, Ramsay writes, was a first-rate analyst, and under him he acquired the routine of analytical practice. Towards the end he was acting as Tatlock's personal assistant. During the winter of 1869—70 he attended Professor Anderson's lectures in the University.

He had by now quite made up his mind to take up chemistry as a profession, and was planning to go to Heidelberg to work under Bunsen when the Franco-German War broke out. He actually visited Bunsen in the autumn, but it was thought wiser to keep away from the Continent for the winter. He filled in the time by attending lectures by Professor Thomson (Lord Kelvin), and working in his laboratory, which was in a cellar. The apparatus was home-made. The prize in Professor Thomson's class, awarded, curiously enough, on the vote of the students, went to Ramsay, though he had been unable to complete the course. This, his one academic honour, meant a great deal to him. He also attended a course of lectures on geology, and one on anatomy. In the meantime he had been advised, probably on grounds of economy, to go to Tübingen to work under Fittig, rather than to Heidelberg. This was unfortunate.

Ramsay has been described as a lucky man. He was certainly very lucky in his parents, and in his early environment; but, as I

have shown, the position in which he found himself at the age of seventeen was mainly due to the use which he had made of his opportunities. He was not lucky in the advice which he was given as to the choice of a foreign University, nor was he lucky in any of the opportunities which offered themselves during the next ten years of his early manhood. His first luck came with his appointment to the Chair of Chemistry in University College, Bristol, but then circumstances forced him into the position of Principal of the College. It was not till he had settled down in University College, London, at the age of thirty-six, that he found reasonable facilities for research. In 1870 he should have gone to Heidelberg, where, under the leadership of Bunsen, amongst the personnel that such a man collects around him, there would have been the best opportunity for the development of that genius that was in him. Yet, Fittig was a master of the methods of organic chemistry, and while Ramsay might have done better at Heidelberg, he still did well under Fittig, carrying out a sound piece of research, and sharing with one other a degree in the highest class which was awarded for such work.

The first thing Ramsay did on arriving at Tübingen was to hire a piano. He worked hard and played hard. He made a lot of friends, some of them from amongst the American student community, which was large enough to form a baseball club. Ira Remsen, Fittig's assistant, afterwards President of Johns Hopkins University, remained a life-long friend. He played billiards for an hour in the evenings, and mentioned it in one of the many letters to his mother which still exists. It took a long letter afterwards to explain to her that it was not as wicked as it sounded, that he had no intention of giving up playing billiards in Germany, or of continuing to play billiards when he got back to Scotland. He took long walking tours through Southern Germany and Austria, exploring the Western Tyrol; and he then began a series of letters, written first to his parents and in later years to his wife, which told of his daily adventures in work and play. These are fascinating reading. Many of them were made use of by Sir William Tilden. A collection of them has been made, and it is hoped to publish a selection of them sometime.

Just before Ramsay returned to Glasgow in August, 1872, some remark that he made in a letter led his father to raise the question, "Was his son really wise to take up chemistry as a career?" But Ramsay adhered to his intention, and about this time he accepted the appointment of Assistant to the newly appointed

Young Professor of Technical Chemistry in Anderson's College, the forerunner of the Royal Technical College, Glasgow. The appointment was not a happy one. The Professor, Bischof, never learned to speak English, and the department was run by Mr. Young, the founder of the Chair. Ramsay proposed to him that he should give a course on organic chemistry. He writes, " The answer came sharp and bitter, ' I do not consider that organic chemistry has anything to do with technical chemistry, and I consider that it would be interference with the work of other Professors '."

It may be remarked that the idea that a Professor might lay down his own courses, much less hold his own class examinations, had not yet developed, and when Ramsay became Principal of University College, Bristol, he had to demonstrate the absurdity of expecting the Principal to read a certain proportion of the answers of the students to the examination papers in all departments.

Ramsay had intended, apparently, to carry on in Glasgow some work which he had commenced at Tübingen, but Young's veto put an end to this. He carried out a small piece of work on antimony phosphide, with R. W. F. MacIvor, who afterwards went to Australia, and attained some distinction in agricultural chemistry. He found a life-long friend in Otto Hehner, afterwards a leading London analyst, who wrote in 1916, " At the Anderson's College we were first confronted with the Sprengel pump, which became an important instrument in Ramsay's epoch-making discoveries ". Bischof was only a bird of passage, and he was succeeded by E. J. Mills, " A very able man, who has raised the status of the place. . . . I often see and talk with him." But in 1874, his friend Ferguson, Professor Anderson's assistant at the University, succeeded his chief in the Chair; and before the appointment had received the Royal approval Ramsay was applying for a post under him. He was appointed tutorial assistant, hardly an enviable post, but the openings for young chemists were few. The work consisted in holding coaching classes for 200 medical students, divided into four groups, each group meeting twice a week. There were also test papers to be marked. In one session he gave a course in organic chemistry; it was not well attended. In 1876 he writes, " I am giving a course on chemical geology, which is not a very well understood subject. It takes me all my time to grind up the facts, and to evolve the theories."

Ramsay's heart was still in organic chemistry, and an opportunity offered to carry out some interesting work. Professor

Anderson had spent a lot of time in fractionating Dippel's bone oil, and the products were stored in the University cellars. Ferguson regarded these as museum specimens; but Ramsay persuaded him to allow him to use part of them for further work. It had already been shown by Dewar that pyridine was a tertiary amine, and was related to benzene by the replacement of one CH by N. Ramsay spent the next three years in studying the picoline fraction in particular.

He found in McKendrick, the Professor of Physiology, a kindred spirit, and with him studied the pharmacological properties of the compounds which he obtained. This led to the investigation of some alkaloids, and this research carried out with a student, James (afterwards Sir James) Dobbie led to the discovery that these compounds, when oxidised with alkaline permanganate, yielded acids similar to those derived from the pyridine bases. This investigation forms the basis of later work on the alkaloids.

Ramsay was twenty-four at the time, and Dobbie was not much younger, but he must yet be regarded as the first of the line of junior colleagues who, in turn, were associated with Ramsay in his researches. Each in turn contributed to the success of Ramsay's investigations, as he was always the first to admit; but each of them paid tribute to his power of leadership, and regarded him as their revered and also beloved chief.

Sometime about 1876 Ramsay came into contact with a very remarkable young man, J. B. Hannay. He was rather more than two years younger than Ramsay, but he had left school at the age of fourteen to help his father, who owned the Theatre Royal, Glasgow, and had been employed in making coloured fires to produce scenic effects. This had led him to study chemistry, which he had done most enthusiastically. At the age of eighteen he had already contributed some short, but interesting, papers to the Chemical Society. He then joined a chemical manufacturing company, and before he left them, three years later, he had become manager. After this he worked for a short time as assistant, either to Professor Mills or to Professor Dittmar, in Anderson's College, and for a part of one session he was assistant lecturer in chemistry in Owens College, Manchester. He then opened a private laboratory in Sword Street, Glasgow. An outline of his work has been published by the writer (*Chemistry and Industry*, 1939, 507). Ramsay first met Hannay apparently, when he was working at Anderson's College, and they collaborated in a research arising out of Ramsay's studies in

geological chemistry. It involved the determination of the rate of loss of water by hydrated salts. In 1878 Hannay was carrying out some experiments with an apparatus which he had invented and called a microrheometer, which is practically the well-known Ostwald viscometer. He made all the glass apparatus himself, and Ramsay, wanting one of these instruments, tells McGowan that he stood by and watched, while Hannay made it for him. At this stage it is clear that Hannay was a highly skilled glass-blower, while Ramsay was not. Till he met Hannay, Ramsay's work had lain entirely in the field of organic chemistry, but about this time he was turning to what we should now call physical chemistry. This was a field in which Hannay was already a master worker. Anyone who reads his papers in the *Proceedings of the Royal Society* between 1878 and 1880, when he abandoned scientific investigaton for industry, cannot fail to recognise the fact that he was a brilliant experimental investigator.

In 1876 the British Association visited Glasgow under the presidency of Professor Thomas Andrews of Belfast. Ramsay wrote, in a letter to George McGowan, a glowing account of the meeting. He was thrilled by the experiments of Osborne Reynolds on the flow of fluids past obstacles, but he made no mention of the President, or of his classical work on the critical state, which, curiously enough, the President himself did not mention in his Address. The inspiration for the work which both Hannay and Ramsay were soon to take up came, probably, from James Thomson, who had been appointed Professor of Engineering in Glasgow in 1873. He had been associated with Andrews in Belfast, and had published two interesting papers on liquid–vapour systems in the British Association Reports of 1870—71. Hannay published a short and a long paper in the *Proceedings of the Royal Society* in 1879—80 entitled " On the Solubility of Solids in Gases ", in which he shows that there is no discontinuity in the solubility of solids in fluids above and below the critical point. In the longer paper he describes in detail the modification of the Andrews apparatus afterwards used by Ramsay and Young in their work on liquid–vapour systems. He followed this up by a series of papers on the critical state. Of these, two in particular, read before the Royal Society in May, 1880, and in March, 1881, are of particular importance. In them he shows that the rise of a liquid in a capillary tube decreases with rise of temperature, and becomes zero at the critical point. This he considers to be the criterion of the limit of the liquid state. In February, 1880,

and in November of the same year, Ramsay contributed papers to the Royal Society criticising Hannay's experiments and conclusions, describing experiments of his own. These are, however, clearly vitiated by the fact that his attempts to secure the uniform heating of a long capillary tube by allowing it to rest in a groove in a heated copper block, so that it was exposed on one side to the air, were ineffective. The variation in the temperature of the tube along its length gave rise to phenomena which he regarded as evidence of the co-existence of vapour and liquid matter in different states of molecular aggregation, as he believed, above the critical point. This work was discontinued till he had been for a year in Bristol as Professor. He had come late to this kind of work, and it took him a little time to be wary of the pitfalls which beset the footsteps of those who are over-bold in venturing on difficult problems in physical chemistry.

We left Ramsay, a little way back, still tutorial assistant at Glasgow University, finding the burden of the work wearying. However, his life was not all work and no play. He still had some time for research, and in the holidays he travelled far and wide, attending meetings of the *Association Française pour l'Avancement des Sciences*, and making acquaintance with many of the leading continental chemists, with whom he could converse and correspond in French and German. Many of them wrote recommendations for him when he was applying for posts. He applied for Chairs of Chemistry vacant in Dublin, in Belfast, and in London, and at the age of twenty-eight was feeling a little discouraged. Then the Chair of Chemistry in the newly created University College, Bristol, became vacant, and in 1880 Ramsay was elected to it. The salary was guaranteed at not less than £400 a year (it was only £350 in 1904), and there were evening classes to be given in the College as well as lectures in Stroud and Trowbridge for the benefit of the dyers. Ramsay may have had chemistry in his blood, but his ancestors had not transmitted to him a knowledge of the art of dyeing, and he was at some pains to study the subject. He went to Bristol in March, and soon made friends with the group of very able men who formed the staff. These included Alfred Marshall, economist, S. P. Thompson, physicist, W. J. Sollas, geologist; and, a little later, Lloyd Morgan, geologist, naturalist, and a founder of experimental psychology, joined the staff. Although University College was not well supported financially, the staff were held in high esteem in Bristol, and the activities of the Colleges were always

well reported in the Press. Ramsay had the right to appoint an assistant, and for this post, worth £150 a year, he selected David (afterwards Sir David) Masson, Professor of Chemistry in Melbourne, and a life-long friend. Writing of Ramsay in 1934 and referring to the caricature of him by " Spy " he says, " To me it suggests Ramsay as I knew him—keen, clever, humorous, and a most delightful and stimulating companion. . . . I have always thought that to understand Ramsay's character, career, and achievements, one must first realise that he was at the same time extraordinarily self-reliant, and yet free from self-conceit. If he wanted to do anything that struck him as worth while, no difficulties, however great, would stand in his way, if anything he was more attracted to the task. I do not think he ever contemplated failure, nor was he ever deterred by shyness of other people's opinions. He could respect criticism that was well-founded, but otherwise it left him cold, and he simply passed it by. Next, one must realise that he was by nature quick-witted, a rapid worker, yet endowed with more than normal patience when patience was called for. . . ."

Masson came home frequently from Australia, and kept close touch with Ramsay, and in 1895 the two families stayed for some time at Kilcreggan on the Clyde. His son, now Vice-Chancellor of Sheffield University, writes of that holiday fifty years ago, " . . . there remains in memory too much for this brief note; but Ramsay, happy in a boat, Ramsay whistling an aria brilliantly, Ramsay cracking jests with William Macnab, genial and placid, and Ira Remsen, gravely humorous; Ramsay half-embarrassing and half-delighting a small boy by a mock solemn address of thanks for a long birthday excursion to Loch Lomond; Ramsay singing 'In the North Sea lived a whale', or the chorus, beyond the compass of the Sassenach tongue, 'Wi' a Heuch Ay, Heuch Ay, Camlachie, Ecclefechan, Auchtermuchty, and Milngavie'; Ramsay entering with full zest into a children's fancy-dress party; Ramsay talking deep chemistry to other men—these are all part of it." The boy was to work under Ramsay as a student, and to be the last of Ramsay's young collaborators, as his father had been the first but one.

Masson stayed with Ramsay for a year only. He then returned to Edinburgh. He was succeeded by Adrian Blaikie, to whom Ramsay became closely attached, but whose health did not stand up to the strain of the work. Blaikie, in turn, was succeeded in 1882 by Sydney Young, who had held a junior appointment on the staff

of Owens College, Manchester. In the meantime two events had happened. In the year following Ramsay's appointment as Professor, the Principalship of the College became vacant, owing to the resignation of Marshall, and before the session opened in the autumn Ramsay had been elected to the post. The additional stipend was £250; and, in anticipation of the appointment, he had married Margaret Buchanan in August. Of their home life and hospitality I shall speak later, only remarking that Ramsay's home life and professional and scientific activities had always been inseparably connected. The story of his daily life, down to his engagement, is told in his letters to his parents and his friends. In April, 1881, the letters to his parents become a little less frequent, but a new series of letters opens. When these came into the hands of the writer, all carefully arranged and docketed, he hesitated to read them till he had been assured by Ramsay's daughter, Lady Tidy, of the truth of a remark made by Ramsay in one of them, that he had never become sentimental on paper. Some day they may be regarded as a mine of information about the life of a scientific man of the period. Curiously enough, his wife was absent, often on a visit to his mother, at the time when some of the work leading to his major discoveries was in progress, and the letters form an authentic source of information as to what actually happened.

Sydney Young was of a type utterly different from Ramsay; but they got on excellently, for Ramsay found that he had an able and reliable colleague. Ramsay had no use for a collaborator on whom he could not rely absolutely, and who would not take responsibility, and go on with the work in hand whether he were there or not. The only criticism that he was ever heard to pass on Young was that it was difficult to get him to talk of anything but shop. Possibly, he never tried to talk to him about roses. However, their scientific interests at the moment were running on parallel lines; for before leaving Manchester Young had become interested in the vaporisation of ice, and in a letter to *Nature* he had put forward an explanation of Carnelley's observation that ice when heated under very low pressure does not melt. He and Ramsay were later to carry out an investigation in this direction. During the five years that they worked together they carried out a series of investigations on liquid–vapour systems and the thermodynamic relationships which they proved to exist. These researches are regarded as chemical classics. It is interesting to note that the work opens with a study of methods of maintaining constant

temperatures. Ramsay had realised where he had gone wrong in his earlier work on liquids and vapours.

In these five years Ramsay had succeeded in building up a research school. Masson and he had continued some work which Ramsay commenced in Glasgow on the molecular volumes of elements and compounds at their boiling points, which aimed at determining the atomic volumes of elements in combination, on the lines indicated by Kopp. With Lt.-Col. H. C. Reynolds, Ramsay determined the equivalent of zinc, by measuring the hydrogen evolved by the action of acid. The work is interesting, as Ramsay's first essay in gas investigation. E. P. Evans, J. Tudor Cundall, and Miss K. Williams also commenced research under Ramsay, and continued to work at research in the Bristol laboratories under Young, when he succeeded Ramsay in the Chair.

The post of Principal was no sinecure. There were internal difficulties, arising in part from strife amongst the staff, and more particularly from the fact that public support was inadequate, and the College was running into debt. The question of reducing salaries arose, and Ramsay offered to accept a reduction of £150 a year. How he meant to face a reduction of income from £650 to £500 is shown in a letter written by his wife; but happily the sacrifice was not called for. Actually, the emergency only stimulated him to an effort to meet it. The question of Government support for University education had often been raised, and seems to have taken concrete form at a meeting of the Principals of the University Colleges held in 1885 at Cambridge at Ramsay's suggestion. It appears to have arisen out of conversation during a trip which Ramsay and his wife made with the British Association to Canada in 1884. However, the three senior Colleges—those of Manchester, Liverpool, and Leeds—held aloof from the decision to take positive action, and the Welsh Colleges, already in receipt of a Government grant, were content with things as they were. A meeting of the Principals of the English Colleges was held in London in April, 1886. A Committee was formed, with Hicks (Sheffield) and Ramsay as secretaries and conveners. Much correspondence passed between Ramsay and Dr. Jowett, Master of Balliol College, Oxford, and also various politicians, and the campaign was definitely opened by a strong letter from Dr. Jowett, which *The Times* published with a leader in support of it. This was followed by a letter from Sir Henry Roscoe. We cannot follow the story here. Success was not achieved immediately; but in 1889, as a small beginning, a

grant to the University Colleges of £15,000 was included in the Budget. Ramsay wrote about it, "I hope Bristol will get a good slice. Even £1000 would be a relief to them."

It may be noted that the association with a capable colleague in his research work freed Ramsay to undertake work such as this, which was not one of the least of his contributions to the advancement of science.

In 1887 Ramsay was elected to the Chair of Chemistry in University College, London. This was where he hoped to be, for contact with fellow scientists was the spice of life to him, and everyone came to London. The burden of an endless stream of visitors was to drive him from London twenty-five years later. So far as work was concerned, it was beginning all over again; for though his predecessor, A. W. Williamson, had done distinguished work in the fifties and sixties, he had stayed at his post too long, and the place required complete reorganisation. The main laboratory was a long shed; adjacent to it and dimly lit by gas-burners at night, were a number of basement rooms, stacked with boxes, bales, jars, and bottles, nearly all without labels. A large collection of copper stills and curious glass apparatus reminded one of alchemical days. When the writer joined the department three years later the clean-up had made progress. Ramsay and his two assistants, Richard T. Plimpton and J. Norman Collie, had brought some order into the place, and a good deal of research was in progress. Ramsay in London and Young in Bristol were, independently, following up lines of work arising out of their studies in vapour–liquid systems, and Ramsay was preparing to follow up some ideas which he had had in mind for some time, and to investigate the molecular aggregation of liquids by studying the variation of surface tension with temperature. In this work he was associated with Dr. John Shields. Collie was engaged in research in organic chemistry, paying particular attention to compounds containing $-CO{\cdot}CH_2{\cdot}CO-$groups. Plimpton was studying the metallic compounds of acetylene. Other interesting researches were those of Picton and Linder on the cataphoresis of colloidal solutions, and of Miss E. Aston on the atomic weight of boron, and of Miss D. Marshall on the heats of evaporation of organic liquids. E. C. C. Baly, afterwards Professor in Liverpool University, one of the first students to enter the College under Ramsay, was carrying out some researches on the behaviour of gases under low pressures. He excelled us all, even Ramsay, as an amateur glass-blower. Looking back on those

days, the fact that strikes one is that, after a certain efficiency in qualitative and quantitative analysis had been attained, and a number of inorganic and organic preparations carried through, there was no fixed course of laboratory work. Ramsay made a round of the laboratory almost every day, often suggesting a departure from a routine method of carrying out some operation. A favourite form of exercise for him to set a student was to repeat something described in recent literature. This remained Ramsay's method of conducting a laboratory to the end. Sir A. C. Egerton writes, " All the time working under his guidance as an undergraduate was a sheer delight to me. He used to bring me things to do for him specially; one was an investigation on the crystallisation of copper sulphate, supposed to contain lithium. This was in connection with his work with Cameron on the supposed transmutation of copper to lithium. Though it led to a false issue, it led him to be the first, or one of the first, to use microchemical methods of analysis." J. I. O. Masson, writing of Ramsay's last days at University College, says, " He put me on to try whether the photoelectric effect on a metal was in any detectable degree irreversible, in the sense that the loss of one electron might perhaps transmute one atom of an element into an atom of another. It was, at that date, one of those ideas to which Ramsay's characteristic ' it is worth trying ' applied in the very spirit which led him, against expectation to add a whole new and unexpected group to the Periodic Table." Above all, everyone was expected to know about what was going on around him. On one occasion the candidates for an internal scholarship examination were astonished on taking up the paper to read the words, " Give an account of any of the researches being carried on in this laboratory with which you are acquainted ". That they could do so was due to the fact that senior students and research workers were not separated, that the numbers were few, and there were no private rooms.

In 1881 Ramsay was elected a Fellow of the Royal Society. After that he was a regular attendant for tea at the Thursday afternoon meetings, frequently taking members of the staff, or research workers, with him.

Of those early days at University College Baly writes, " It was a pleasing custom of Ramsay to invite us to dinner at his house. It was rare for any distinguished foreign chemist to visit London without being the guest of the Ramsays. I was especially fortunate to meet at their house Mendeléef. His presence and personality

were truly remarkable; but unfortunately he could only speak French and Russian, and Ramsay had to act as interpreter. It was an unnerving experience to confer with the great man in this way, and I must confess that it cramped my style badly. But Mendeléef soon broke down the barrier, and held a group of us around him enthralled." The Saturday evening dinners remained an institution, certainly till the writer left London at the end of 1903. After dinner there was some conversation round the dinner-table, and then we went to the drawing-room, where we all had to sign our names in a book. Ramsay and his wife were ideal host and hostess, whether entertaining distinguished company or a group of students. According to custom, we called in the afternoon a Sunday or two later, when there was tea and more conversation, and the opportunity of meeting some of their non-academic, but pleasant, and often distinguished friends. Perhaps the greatest piece of good fortune which could happen to any of his junior colleagues was to accompany Ramsay on one of his trips to the Continent. It was the writer's good fortune to be with him in Berlin, in Paris, and in Leiden. Ramsay was on terms of intimate friendliness with so many of his foreign colleagues that these trips had quite a unique character. There were lectures and scientific meetings to attend; but memory lingers around the quiet family parties at which we were guests. In one visit to Berlin we were taken by Emil Fischer, Ramsay's closest foreign friend, round his new laboratories, we were entertained by the science masters at a dinner which ended in the early hours of the morning, we drank a bottle of wine with Kohlrausch in his private room at the Reichsanstalt, and we lunched *en famille* with the van 't Hoffs.

The story of the discovery of helium, neon, argon, krypton, and xenon has been told by the writer in some detail in "The Discovery of the Rare Gases", published in 1928, and it could be amplified considerably by the addition of material which came to light after the death of Lady Ramsay in 1936. In September, 1892, in a letter to *Nature*, Lord Rayleigh had called attention to the difference which he had observed between the density of atmospheric nitrogen and nitrogen from chemical sources, asking for suggestions as to the cause. No definite suggestion appears to have been put forward. The details of Lord Rayleigh's experiments were published in a paper read at a meeting of the Royal Society on April 19th, 1894, but the paper contained no suggestion as to the cause of the discrepancy or indication that steps were being taken to clear it up.

There was some conversation between Lord Rayleigh and Ramsay, who suggested that the answer might be given by a chemical investigation, which he proposed to carry out. This was to absorb atmospheric nitrogen by red-hot magnesium, and to see if anything were left. Ramsay was acquainted with the Cavendish experiment at the time.

In the course of the month of May, Ramsay's assistant, Percy Williams, passed atmospheric nitrogen over hot magnesium, and found that as the absorption of the nitrogen proceeded the density of the remaining gas increased. Then, early in July, when the examinations were over, Ramsay took the work in hand himself, and, after having passed about 23 litres of atmospheric nitrogen over magnesium, obtained a residue amounting to about 1½ litres. This was passed backwards and forwards through a train of tubes containing solid potash, phosphorus pentoxide, and heated magnesium and copper oxide, the volume being reduced to about 200 c.c. in the process. After some further treatment the volume was reduced to about 150 c.c., and the density was then determined under slightly reduced pressure in a bulb holding 163 c.c. It was found to be very close to 20, that of oxygen being taken as 16.

The best account of the work carried out in the month of July is given in a paper which Ramsay wrote between August 4th, when he wrote to Lord Rayleigh telling him about it, and August 7th, when he received Lord Rayleigh's reply, telling him that he, also, had isolated the gas by Cavendish's method, but in too small quantity to do anything with. The manuscript is headed " On a new gas contained in air. By William Ramsay, Ph.D., F.R.S." Ramsay had written to Lord Rayleigh on May 24th, telling him of his first experiments; but Lord Rayleigh's letter of August 6th was the first intimation that he was repeating the Cavendish experiment. While each of the investigators was prepared to withdraw in favour of the other, they quickly decided that " joint publication was the only solution ". Ramsay put his manuscript aside, and the writer saw it for the first time forty years later when looking through the papers left by Lady Ramsay. It refers to the work of Cavendish and to that of Lord Rayleigh, and describes in some detail the method of preparation of the new gas. It describes some experiments on sparking with oxygen, and an attempt to examine the spectrum, which appeared ill-defined. It concludes with some observations on the position of the gas, if an element, in the periodic series.

A joint announcement of the discovery was made to the British Association at Oxford on September 13th, 1894. It raised a great deal of interest, and called forth an even greater amount of comment and criticism, doubts being thrown on the accuracy of the work and on the validity of the conclusions. No notice of the various letters and newspaper articles was taken by either of the discoverers.

In the autumn the work was taken up again, the first entry in Ramsay's notebook being August 18th. Amongst the last entries in the notebook before the holiday is one which is rather amusing, and another which is the reverse. The first is, "Dreamed that owing to the dryness of the soda lime and the gas, it might have consisted of CO_2, unabsorbable with dry soda lime. At once tried it with strong potash solution. No absorption whatever. . . ." The second tells how, when he came to the laboratory in the morning, he found that the reservoir had cracked round the top, as such pieces of glass apparatus do when unannealed, and practically the whole of the new gas was lost. So the first thing to do when work began again was to make some more of the gas, now called argon. The writer, to whom Ramsay had just given a junior appointment, calling at the College towards the end of September, found him engaged in this work in one of the basement rooms, and was greeted with the words, "Well! It's a new element."

On January 31st, 1895, a joint paper was read by the discoverers before a special meeting of the Royal Society held in the lecture theatre of the University of London in Burlington House. Ramsay was the speaker. Lord Kelvin, as President, was in the chair, and the place was crammed. After their long silence everyone was anxious to hear the details of the discovery, the importance of which was recognised. Lord Kelvin was critical of the conclusion that the gas was monatomic, which was drawn from the value of the ratio of the specific heats. Professor Armstrong recommended caution in accepting many of the statements put forward. However, the meeting was enthusiastically appreciative of the work of the two authors, and none thought of raising a question, which some still seem to think important, and others of no importance at all, which is —Did Cavendish, Rayleigh, or Ramsay really *discover* argon?

The story of the discovery of helium may be told briefly. It begins with the discovery of the line D_3 in the sun's spectrum by Mr. (afterwards Sir Norman) Lockyer, in 1870. Then came the discovery by Hillebrand of the fact that certain minerals, on heating, evolved a gas which was neither hydrogen nor carbon dioxide.

The day after the paper on argon was read, this fact was called to Ramsay's attention by Mr. (afterwards Sir Henry) Miers. Ramsay, when he had cleared up current matters, bought a sample of the mineral, cleveite, and obtained a gas which gave a remarkable spectrum, which many, including the writer, claim to have been the first, after Ramsay, to see. A Plücker tube filled with the gas was sent to Mr. (later Sir William) Crookes, who photographed the spectrum and wired Ramsay saying that the spectrum of the gas included the helium line. The gas therefore was, or at least contained, the celestial element to which the name helium had been given by Lockyer. A few density determinations were carried out, and a preliminary paper was sent to the Royal Society. The end of the term then came, and Ramsay invited Norman Collie and Morris Travers, who had joined the staff in the previous autumn, to cut short their holiday in Scotland, and to come back to the College to help him to work on the gas. A paper on the preparation and properties of helium was read in their joint names at a meeting of the Chemical Society in June, 1895.

In dealing with an historical problem of this kind the real difficulty which the student has to face is in adopting the outlook of the time *of* which he is writing. It is difficult to avoid slipping back, quite unconsciously, into the time *in* which he is writing, and in endowing his characters with knowledge which they did not possess, or certainly did not make use of. This applies less to facts than to generalisations, which are at first too often received with incredulity, or even with ridicule by the majority. Whether a particular individual was able or willing to make use of what was certainly knowledge at the moment is often very difficult to determine. Thus, in the late seventies it is certain that neither Ramsay nor Hannay knew of the work of van der Waals, first published in 1873, and it was only when Ramsay reopened his investigations with Young that he appreciated its significance.

However, Ramsay could not be considered to be slow in adopting new ideas, and though in the late eighties the *periodic law* could hardly be placed in this category, it seems still to have been regarded by most chemists as a curious and interesting relationship, but without any fundamental significance. To appreciate this statement one must bear in mind the fact that progress had been mainly in organic chemistry, to the neglect of inorganic chemistry, and that side of the subject which was to be called physical chemistry. But the formulation of it had possibly accentuated the importance

of the question, "Was there any truth in Prout's hypothesis?", and a number of distinguished chemists had devoted their lives to attempting to answer it by carrying out very accurate determinations of the atomic weights. It was to answer the same question that Lord Rayleigh undertook his investigation into the densities and compressibilities of the principal gases, which led up to the discovery of argon. Ramsay was the first to base a text-book on the periodic system of classification, and he made this book the basis of the lectures to his general class. The *periodic law* was the basis of the investigation which led to the discovery of the series of rare gases.

In the original paper on argon, when he, if not Lord Rayleigh, had come to the conclusion that argon consisted mainly of a single monatomic element, Ramsay did not go farther than to discuss its possible position in the *periodic table*. That it seemed to possess "no valency, that it was incapable of forming a compound, or, if forming one, being an octad" made it reasonable to suppose that it should be placed in the eighth group, between chlorine and potassium. But the abnormality in the atomic weight was unique; for the corresponding abnormality involving iodine and tellurium was generally discounted, and was not evidence. The discovery of helium increased the probability that helium and argon were members of a new eighth group of elements.

It was not till much later that Ramsay committed himself to a definite statement on the subject; but in the first edition of "The Gases of the Atmosphere", published in 1896, he reproduces the *periodic table* in a form suggested by Masson of Melbourne. The significant part of it is set out below.

Hydrogen	1·01	Helium	4·2	Lithium	7·0
Fluorine	19·0	?		Sodium	23·0
Chlorine	35·5	Argon	39·2	Potassium	39·1
Bromine	79·0	?		Rubidium	85·5
Iodine	126·9	?		Caesium	132·0
?	169·0	?		?	170·0
?	219·0	?		?	225·0

He does not commit himself to any speculations as to the significance of the notes of interrogation. However, by this time he was fully convinced that the eighth group would certainly be found to include three inactive gases, with atomic weights close to 4, 20, and 40, and possibly, but not with equal certainty, there would be found members of the series with higher atomic weights. It was not till 1897 that, in his brilliant address to the Chemistry Section of the British Association in Toronto, under the title "An

Undiscovered Gas", he made public the ideas which guided the investigations which he carried out in University College, London, during the last six years of the century.

The first question to be answered was, "Are helium and argon homogeneous?" This was attacked by submitting the gases to fractional diffusion, and from the results of the experiments it was concluded that neither of the gases contained a heavier or a lighter constituent in detectable proportion. Then the problem resolved itself into a search for the missing element or elements, and in this work Ramsay invited Morris Travers to join him. This was early in the year 1896. It was four and a half years before the work was brought to a conclusion.

It began with investigations into the nature of the gases from mineral springs and obtained by heating minerals, meteorites, etc. Some years later Ramsay thought that he had detected neon in the gas from the hot springs at Bath, but it is now quite certain that the quantity of argon and neon in the gas is not more than can be accounted for by atmospheric contamination. Helium is the only one of the gases which is known to be given off from the earth, or which is present in minerals in quantities which can be detected by methods hitherto employed, and that Ramsay and Travers failed for some time to find the missing element was only because they failed to look for it in the right place, in the air around them.

After a somewhat desperate attempt to separate an inactive element, which might be a liquid at ordinary temperatures, from sea water, they came to the conclusion that the only thing to do was to make more careful examination of helium and argon, to see whether those gases contained traces of the missing element or elements. Of helium, a considerable quantity was already available; and it was decided to make fifteen litres of argon, and to liquefy it using liquid air made by a process which was being developed by Dr. W. Hampson and Mr. K. S. Murray of the British Oxygen Company. But before the argon was quite ready, a small quantity of liquid air, the first ever available at University College, was obtained, and the gas from the last cubic centimetre of it was collected. After removal of the oxygen and nitrogen from it, a residue was obtained which gave a spectrum with a very bright green line, and a bright yellow line which did not correspond with either the sodium or the helium line. The gas proved to contain much argon, but the density was 22·5, that of argon being close to 20, so it seemed clear that the gas contained one of the heavier members

of the series, and not the element which should fill the place between helium and argon. It was named krypton.

This discovery was made on May 31st, 1898. A few days later the preparation of the argon was complete, and it was condensed in a glass bulb cooled in liquid air boiling under reduced pressure. When the whole of it was liquefied a small quantity of the most volatile fraction was collected. This was freed from traces of impurity and introduced into a vacuum tube. Now it was already well known that atmospheric argon contained a trace of helium, and this gas, or some other light constituent if such were present, should now be detected. When the current was turned on the blaze of crimson light from the tube showed that the *unknown gas* of the Toronto Address really existed. It was given the name *neon*. This was in June, 1898.

But it was one thing to detect these gases in the atmosphere, and quite another to isolate them and measure their properties. This took two years. Measurements of density and of the refractivities were used as criteria of the progress of separation of the gases. Though Dr. Hampson and Mr. Murray helped as far as they could, it was only possible to obtain liquid air late in the evening, and work had to be carried on far into the night. However, in the spring of 1899, Mr. Rose Innes and Mr. Ludwig Mond presented the College with a liquid air apparatus, and this helped enormously. But the work of collecting and working up heavy and light liquid air fractions was laborious. It was soon found (in July, 1898) that the heavy fraction contained a constituent heavier than krypton, to which the name *xenon* was afterwards given. This seemed to be the last member of the series which was present in air in detectable quantity, so it proved comparatively easy to separate pure. In a year, about 3 c.c. of the gas had been collected, and this proved to be sufficient for the determination of the physical properties. The atomic weight from the density determination was 128, which fixed its position in the periodic table. The accepted value of the atomic weight is 131.

Krypton was more difficult to separate, as it was mixed with a lighter impurity, argon, and with a heavier one, xenon. Ultimately, two fractions each of about 6 c.c. were obtained, of which it was written in the paper published in 1901, "We considered, therefore, that since we had succeeded in separating by fractional distillation from a lighter and heavier impurity respectively two samples which agreed in two distinct physical properties, we were justified

in assuming that we had isolated a definite chemical substance ". The density determinations corresponded to atomic weight values 81·64 and 81·46 (83·7 at present accepted). The refractivities were 1·450 and 1·449, air = 1.

It was soon found that the light fraction of the gas contained both argon and a considerable quantity of helium, and all attempts to separate pure neon from the heavier and the lighter impurity failed. The trouble was that as soon as the argon content fell below a certain limit it was quite impossible to liquefy the gas, even by using liquid air boiling *in vacuo*. Various other methods, such as fractional solution in liquefied gases, proved ineffective. The only obvious method of attacking the problem appeared to be to use liquid hydrogen, but no liquid hydrogen was available. Early in the year 1900, Travers undertook to try to liquefy hydrogen, making use of the compressor of the liquid-air apparatus, with a gas-holder and such accessory apparatus as could be made or purchased for £50. A small liquefier was designed and made, a gas-holder was purchased, and arrangements for generating hydrogen were extemporised. Early in July about 60 c.c. of liquid hydrogen were obtained. The mixture of helium, neon, and argon was introduced into a bulb cooled with the liquid. The helium did not condense at all. The neon condensed to a slightly volatile solid, by the evaporation of which pure neon was obtained (in July, 1900), the argon being non-volatile. The final experiment took but a few minutes. The values of the atomic weight from two density determinations were 19·98 and 19·88. The accepted value is 20·2. Below these figures in the notebook Ramsay wrote " Q.E.D." This brought the work of six years to a successful conclusion.

It is not possible to do more than mention other work, and other individuals working in the laboratory, during these years. James (afterwards Sir James) Walker, Professor in Edinburgh, had been on the staff for a couple of years, leaving in 1894. Norman Collie had obtained the Chair of Chemistry in the Pharmaceutical Society's Laboratory in 1896, returning to University College as Professor of Organic Chemistry in 1902. Wallace Walker came to London for a couple of years, and then went on to Toronto. In 1900 the staff consisted of Ramsay, M. W. Travers, E. C. C. Baly, and F. G. Donnan. Travers, after the conclusion of the work on the rare gases, continued to work on liquid hydrogen at extreme low temperatures, till in 1903 he was appointed to Ramsay's old chair in Bristol, going afterwards to India. Baly developed a sub-department in

spectroscopy, becoming afterwards Professor in Liverpool; and Donnan, whose main interests were in thermodynamic studies, was shortly afterwards appointed to a Chair in Dublin, and passed thence to Liverpool, ultimately returning to fill the Chair in University College, London, when Ramsay resigned from it in 1912. In the year 1900 the department was still a very small one, though not so small as, from the point of view to-day, the size of the staff would suggest.

On completing the work on the rare gases, Ramsay spent four months in India, where he had gone to advise on the creation of a technical research institution, which a wealthy Parsi, Mr. J. N. Tata, proposed to endow. He and his wife had a most delightful trip, but he did not succeed in getting very far towards sorting out the tangled controversy which surrounded Mr. Tata's scheme. His letters to friends at home are good reading: one to Travers, is published in Tilden's "Life of Ramsay", but space does not permit of quoting from any of them here. He returned home at the end of March, 1901. The Royal Commission on the Disposal of Sewage had engaged much of his time since 1898, and he had done much work, largely of the nature of propaganda, in connection with the reconstruction of the University of London. He was fighting for freedom for the teachers to lay down their own courses of study, and to have a large share in the conduct of the examinations, without the cramping influence of external examinations. His knowledge of universities and university professors all over the world provided him with information which few possessed; and it may seem strange, though it is true, that he found that the most difficult people to convince were the British University professors themselves. That the London schools won a large measure of academic freedom was largely due to Ramsay.

After his return from India, Ramsay stood aside from research for a bit, taking a little time to clear up arrears of personal business. But he spent a good deal of time in the College, and if anything exciting was to the fore, such as a liquefaction of hydrogen, he was sure to be on the spot. His next important venture was in collaboration with Frederick Soddy, afterwards Nobel Prizeman and Professor at Oxford. Dr. Soddy has written an account of this work. It has been necessary to summarise this, but a part, in quotation marks, is given verbatim.

Soddy's association with Ramsay began as examiner and examinee in the Oxford Honours School in Chemistry, when, contrary to

custom, a searching *viva voce* brought Ramsay into contact with all the members of the class, whatever the quality of their work had been. In spite of the circumstances Soddy acquired a great liking for Ramsay, and followed with enhanced interest the work of the previous four years, which started with the discovery of argon by Ramsay and Rayleigh and was rapidly extended by Ramsay, with Morris Travers as collaborator, to the whole of the new period of non-valency elements. But after the establishment of the theory of the atomic disintegration of the radioactive elements by Rutherford and Soddy at McGill University, Montreal, in 1902 these new gases assumed a quite peculiar interest for the subject of radioactivity. This is perhaps the more remarkable as being the only part of the previously known subject of chemistry of which as much could be said then, or even now.

"As we now know, the discovery of the rare gases, by completing the *periodic table*, put the coping stone on the atomic theory. A totally new kind of matter, a completely chemically inert family of new elements, had suddenly been inserted between contiguous, though most violently contrasted of all the families, those of the halogens and the alkali metals. But the full significance of the discovery dawned only gradually, and was not properly appreciated till the first decade of this century had passed, and the *displacement law of radioactive change*, and the *nuclear atom* had deciphered the *periodic law*. The immediate connection in 1902 was twofold. In the first place it had been found that the gaseous products of radioactive change, discovered in the first instance in the case of thorium by Rutherford, and termed the radioactive emanations, were chemically inert gases like argon. Secondly there was an extraordinarily suggestive connection between helium and radioactivity, in that helium alone of the family had been found to exist in large quantity in certain minerals. These minerals had also been found to contain the elements with which radioactivity was associated. The following up of these two distinct clues on the chemical side called for the same technique which had been gradually perfected in Ramsay's laboratory in University College, London, for dealing with the small quantities of gases; though it must be admitted that there was a doubt as to whether these same methods would suffice for the microscopic scale required in experiments with radioactive substances".

"Hence in 1902 Soddy gave up his demonstratorship in McGill University, and, having secured Sir William's interest, he came to

work under him in London early in 1903. He particularly desired the master's confirmation of the suggestion that the emanations were argon gases, and this became easily possible after the radium emanation, now called radon, had been subjected to sparking with oxygen, treatment with hot magnesium, and other standard tests, without perceptible loss. Sir William also wanted to see whether the rare gases exhibited radioactive properties, but these experiments were negative."

The work on radium emanation had become possible by an accidental circumstance. It came to Soddy's notice that the firm of Isenthal & Co. of London were offering pure radium bromide, manufactured from the St. Joachimsthal pitchblends, for 7*s*. 6*d*. a milligram. This was within his means, and he bought 20 milligrams of the product. It may be remarked that, at the time, none outside the Curies' laboratory had been able to obtain a pure radium salt, and then only in very small quantity.

The story continues, " In brief, the hydrogen and oxygen occluded by the salt, owing to the decomposition of its water of crystallisation, were removed by solution, and the gas was passed through a tube cooled with liquid air (in which the emanation was condensed, and again liberated on warming) and transferred to a micro-vacuum tube, which Sir William, no mean glass worker, had made himself. Soddy's enduring recollection of this first successful experiment, in which, by methods previously established, one element was proved to be changing into another, is, that being occupied with the gas manipulation, he was almost the last person in the group to observe the D_3 line of helium in the spectrum of the gas. First Sir William and then Collie, examining the spectrum through a small pocket spectroscope, exultantly announced its presence. And then the room seemed to fill up with staff and students, all eager to get a glance of the spectrum, so that it was difficult to get near to the tube."

Doubt was thrown on the result; but Ramsay was used to having results of work like this doubted. Such criticism didn't interest him.

" The next series of experiments were more crucial, the radium being now in solution, it was used simply to generate radon, and after purification by chemical treatment and condensation in liquid air, so as to free it from helium as well as active impurities, another sample of it was sealed up in a vacuum tube. Helium, absent at first, appeared in the tube after the first day, gradually increasing in intensity, so that after the fifth day, which is approximately the

average life of radon, the whole spectrum was visible. This experiment was repeated many times; but Soddy's abiding impression of the whole subsequent work is one of maddening failure, through insufficiency in the quantity of radium, to map the spectrum of radon itself. As others, who were successful, found afterwards, working with ten times the quantity of radon, this gas possesses the property in common with the rare gases, and particularly of xenon, of 'running out' under the discharge."

"The average life of radon being known, an attempt was made to estimate the average life of radium, by measuring the volume of radon in equilibrium with a known mass of it. In this work the collaboration of a competent mathematician, J. K. H. Inglis, who had come from New Zealand to work with Ramsay was secured. The result arrived at, 1150 years, only differs by a factor of 2 from the accepted value." Soddy concludes, "Certain it is that, had not the rare gases been discovered in the last decade of the nineteenth century, the unravelling of the complex phenomena of radioactivity could not have been achieved in the opening years of the twentieth; and judging from the erroneous speculations about the ultimate constitution of matter current at the time, it is possible that the subject might, like the original alchemy, have become hopelessly bogged."

In 1904 a young German, Otto Hahn, trained in inorganic chemistry in Berlin, entered the laboratory. The story of his work is told by Ramsay in a letter to Emil Fischer in October, 1905, in which he relates how about a year before he had bought 5 cwt. of a radioactive mineral from Ceylon. After the usual treatment the insoluble carbonates were separated, "Then I handed them over to Hahn, who prepared the bromides for the separation of $RaBr_2$. Beautiful crystals of $RaBr_2$ separated; but I noticed that the radioactivity increased not only in the least soluble fraction, but also in the soluble fraction. To cut a long story short it suffices to say that we have a new substance—about 40 mg.—which yields thorium emanation, but which is 250,000 times more radioactive than thorium. . . . Naturally I have talked with him about his problems every day, but I have felt that my part in the work has been so small, that he ought to publish in his own name alone. I have communicated his paper to the Royal Society. This refers to the discovery of radio thorium."

During the last ten years of his life Ramsay devoted much of his time to experimental work carried out with a view to finding an

answer to the questions, "Can the disintegration of elements be effected by chemical or physical means? Is transmutation possible?" No positive results were achieved, but in an essay of this kind it is interesting to consider how it was that the work came to be undertaken.

In 1895 Mach and Ostwald had put forward the theory that the progress of chemistry had been retarded rather than advanced by adherance to the atomic theory, which should be regarded as a convenient method of representing natural phenomena only, atoms and molecules having no reality. All chemical processes could be dealt with in terms of the energy changes associated with them. Ostwald and Ramsay were close friends, and many of Ramsay's research students were from Ostwald's laboratory, so the new idea was given close attention. One may say that it did no more than emphasise the fact that the conception of the atom was indispensable to the chemist. But current ideas as to the nature of the atom were even more unconvincing to the chemist than possibly to the physicist, though it was a physicist, J. J. Thomson, who first put forward a theory acceptable to all alike. This was that the atom consisted of electrons dispersed in an orderly manner in a positive field. It was capable of explaining such phenomena and conceptions as the periodic law, valency, and ionic dissociation. It was not difficult to conceive of such an atom disintegrating with the formation of atoms of elements of lower atomic weight.

Ramsay was undoubtedly strongly influenced by the work of Sir Norman Lockyer, with whom he was closely associated, on stellar spectroscopy and on the influence of temperature on the character of the spectra of the elements. Writing in 1912 in a little book, "Elements and Electrons", in which he sums up his investigations on transmutation, he quotes from Lockyer's book, "Inorganic Evolution" (1900), saying that these experiments had furnished "incontestable arguments that in the sun and stars, bodies believed by us, dwellers in a region of low temperature, to be elementary, split into simpler forms". He summarises Lockyer's arguments.

In 1902 Rutherford and Soddy had first put forward the argument that radioactive change involved nothing less than atomic disintegration, and in 1904 Ramsay and Soddy had shown that this change did not only involve the emission of radiations, with the formation of an element of atomic weight probably comparable with that of the parent element, but that one of the products was an element of very much lower atomic weight, namely helium.

But Ramsay certainly did not visualise at first that anything so dramatic could be effected by external agencies. He seems to have argued as follows. There may be a certain analogy between the decomposition of endothermic compounds and elements generally. Such compounds are generally the more unstable the higher their molecular weight, and some, like radioactive elements, decompose spontaneously. Others, and generally those of lower molecular weight, decompose only under the influence of a stimulus. Similarly, metals, under the influence of ultra-violet light, give off electrons, which in the light of the J. J. Thomson theory is a step in the process of transmutation. He and J. F. Spencer carried out an investigation into the phenomenon, but no evidence of transmutation could be observed, and the matter was dropped.

But in the meantime his work with radon had stimulated exploration in another direction, and he opened the first of a series of papers, in which the work is described, with the words, "The emanation from radium is one of the most potent, if not the most potent chemical agent which exists in nature". He began with observations on the formation of oxygen and hydrogen, together with radon, from solutions of radium in the course of the work with Soddy, and the investigation extended to the study of the action of radon on solutions of salts. In this work he was associated with A. T. Cameron, F. L. Usher, A. C. Egerton, and others. He gave the conclusions which he believed that he had reached in his Address as President of the British Association in 1912. It must be admitted that other workers in the same field have failed completely to confirm his experiments; but it must also be admitted that the object which he aimed at has been partially realised. The sentence in which he sums up indicates the future course of events and must be regarded as prophetic. He uses the words, "It is easily seen that the virtue of the energy of radium consists of the small weight in which it is contained, in other words, radium energy is in an enormously concentrated form. I have attempted to apply the energy contained in niton (radon) to various purposes; it decomposes water, ammonia, hydrogen chloride, and carbon dioxide, each into its constituents, further experiments on its action on salts of copper show that the metal copper is converted partially into lithium, a metal of the sodium column, and similar experiments, of which there is no time to speak, indicate that thorium, zirconium, titanium, and silicon, are degraded into carbon. . . . This leads to the speculation whether, if elements are capable of disintegration, the world

may not have at its disposal a hitherto unsuspected source of energy. . . . If the elements which we have been used to consider as permanent are capable of changing with evolution of energy; if some form of a catalyser could be discovered which would usefully increase their almost inconceivably slow rate of change, then it is not too much to say that the whole future of our race would be altered."

Amongst Ramsay's innumerable extramural activities mention must be made of the founding of the Radium Institute, for which funds were provided by Sir Ernest Cassel. Ramsay had, as a young man in Glasgow, been interested in therapeutics, and his association with the pharmaceutical effect of alkaloids has been referred to. He was also interested in problems affecting the use of anæsthetics. He gave a great deal of his time to the preparation and distribution of radon for the experimental work on the treatment of cancer, thereby sacrificing opportunities for chemical research.

The study of the properties of radon, the last of the series of rare gases, was naturally a subject of intense interest to Ramsay. The difficulties were enormous. It had been possible to collect xenon, a small bubble at a time, from the liquid air used in experiments extending over a year, and to accumulate as much as 3 c.c. of this gas. But only 0·2 g. of radium was available, and the quantity of radon in equilibrium with it was only 0·12 cu. mm., with a half-life of 3·8 days, so that the cases were not comparable. Yet Ramsay and Whytlaw Gray succeeded in 1911 in measuring the density of liquid radon, and also its melting, boiling, and critical points. Comparing the data with those obtained for argon, krypton, and xenon, it appeared that the atomic weight of radon should be 176. According to Rutherford's disintegration theory, radium, of atomic weight of 226, should lose an α particle, or atom of helium, and yield radon of atomic weight 222. Where the apparent discrepancy lay could only be found by actual measurement of the density of radon. How this was accomplished is told by Whytlaw Gray.

"It seemed a forlorn hope to expect a definite result with the small quantity available, but Ramsay was convinced that it could be done. . . . About this time, B. D. Steele, an old student of Ramsay's, working in Melbourne in collaboration with K. Grant, constructed a new form of silica microbalance, sensitive to 10^{-5} mg., and Ramsay seized upon this as likely, with modifications, to be suitable for weighing radon. I was put on to construct a microbalance, and after several trials I made an instrument ten times more sensitive, and

suitable for the purpose. Although various other difficulties prevented the density determination having the same accuracy as the weighing, the mean of the results was very close to 222, the value expected from Rutherford's theory."

These experiments put the crown on the work which had commenced seventeen years before with the isolation of argon.

In the autumn of 1912, when not quite sixty, Ramsay retired from the chair of chemistry in University College. He had already set up a laboratory in his private house in Chester Terrace, where he had some defence against perpetual invasion by visitors. Of his experiences while working with Ramsay on thoria and its products in 1911 Masson writes, " Visitors were numerous from all parts of the world and of varied tongues. One morning I counted ten; and I do not think that anyone but Ramsay could have coupled personal experimenting with such interruptions, as he did, without loss of courtesy to the interruptors, and without ruining bench work." Ramsay planned to break away from all this. His visitors were to be of his own choosing, and with this idea in his mind he bought a house near High Wycombe. He made considerable alterations, converting the stables into a laboratory. But he had only petrol gas to work with, and glass-blowing was practically impossible, so that experimental work of the kind to which he had accustomed himself was also impossible. But he had hardly settled in before war broke out, and putting all purely scientific matters aside he put the whole of his energy into matters relating to the war, either through a Committee of the Royal Society, or through addresses and newspaper articles. Then in the midst of this work he was struck down, and after some months of suffering he died on July 23rd, 1916 in his sixty-fourth year. A great leader was lost; and how truly this was appreciated may be read into a letter written by Sir J. J. Thomson to Lady Ramsay, " I think under the circumstances I may be justified in revealing an official secret, and that is that, as far as I could gather the opinion of the Council of the Royal Society, it was their desire to award him next St. Andrews' day the highest honour in their power ".

The honours which came to him form almost a unique list. They include the K.C.B. in 1902, the Nobel Prize in 1904, doctorates in science in most British and foreign universities, and honorary membership of innumerable academies and scientific societies. Such recognition pleased him, but perhaps even more so the personal letters of congratulations which were associated with them.

He liked to stand well with his fellow men; and it was this quality of unshakable belief in human integrity which drew men to him. Suspicion and distrust were absolutely foreign to him. He hated secrecy, and every visitor to his laboratory was shown all that was to be seen. Never did a student appear to be so worthless that Ramsay had not hopes for him. In his confidence in the work of fellow scientists lay the springs of some of his greatest successes; and the discovery of argon and helium had their origin in his belief that the facts put forward by Lord Rayleigh, Hillebrand, and Rutherford, which were by no means generally accepted, were worthy of careful study. Those who served him had his entire confidence, and he demanded only a confidence in themselves and in him. Late in his life, in a letter to a young relative, he sums up his philosophy of life in two words, " Be kind ".

WILLIAM HENRY PERKIN, JUN.

1860—1929

WILLIAM HENRY PERKIN junior was born on June 17th, 1860, the elder of the two sons of Sir William Henry Perkin by his first wife, Jemima Harriet, daughter of John Lissett. Their second son, Arthur George, was born in 1861, and shortly after his birth, Mrs. Perkin died. About six years later Sir William married Alexandrina Caroline, daughter of Ivan Hermann Mollwo, by whom he had four daughters and one son, the late Frederick Mollwo Perkin.

Of Perkin's early life there is little to record. He went to two preparatory schools, and, at about the age of ten, entered the City of London School, of which his father was a former pupil. He was there from 1870 to 1877; in the ordinary form work he was not regarded as a distinguished pupil, but he took most of the science prizes. As boys, Perkin and his brother Arthur worked in a small hut at the bottom of the garden of their home at Sudbury, which their father fitted up as a laboratory for them. Sir William gave them things to do—crystallisations and such like—but did not attempt any systematic instruction in chemistry, probably very wisely. They were thus brought up in an atmosphere of research, and acquired almost instinctively the feeling that the great object of their lives must be chemical research. Another of Perkin's interests began quite early in life, and was helped if not induced by his environment, for the Perkins as a family were very musical. He started quite early to play on the pianoforte, and by the time he left school played well.

In October, 1877, Perkin entered the Royal College of Chemistry at South Kensington, where he studied under Professor (later Sir Edward) Frankland, and Dr. W. R. E. Hodgkinson, at that time head of the laboratories. At the College he was at once recognised as a student who stood out from all others and was certain to make his mark in chemistry. He had read extensively on chemical subjects, thought deeply about them, and in practical work had the grip of an older student. He soon started on research work under the

[Reproduced by permission of the Royal Society.

W. H. PERKIN, JUN.

direction of Dr. Hodgkinson, and in the latter part of his time at the College he became an honorary assistant in the advanced laboratory, a position he held for nine months. During the vacations he did a good deal of work in his father's laboratory.

Perkin went to Würzburg in October, 1880, to study chemistry under Johannes Wislicenus; he also studied physics under Kohlrausch and mineralogy under Sandberger. His first research, suggested by Wislicenus, did not give a favourable result, and was abandoned. He then started an investigation of the condensation products formed when œnanthaldehyde is treated with potassium hydroxide or other reagents; the results obtained were the subject of several papers and also formed the thesis for his degree of Ph.D., which he received in 1882.

In August of that year he left Würzburg, and in the following autumn went to work under Adolf Baeyer at Munich. The laboratories there were crowded with the most promising men from all parts of the world. Perkin was given a bench in the special laboratory for research students (Saal IV), and his outstanding abilities quickly made him *persona grata* among the élite in the laboratory, which included Otto Fischer, Königs, Friedländer, Bamberger, Curtius, von Pechmann, and others. The work suggested for Perkin was the investigation of benzoylacetic acid and its derivatives, and, although it proved tedious and often very disappointing, the difficulties were surmounted, and it formed his thesis when he passed the examination for Privatdozent. He then took an active part in the teaching work at Munich, and took charge of a large laboratory (in which he also carried out his own researches).

Perkin had not been long in Munich before he felt strongly tempted to try to effect the synthesis of rings containing less than six atoms of carbon. The idea generally held at the time was that carbon rings containing three, four, or five members were not capable of existence, and Perkin entered on the work with little encouragement at first from Baeyer and against the advice of Victor Meyer and Emil Fischer, with whom he discussed his views. The work was brilliantly successful, and Perkin published a series of papers describing numerous derivatives of compounds of this type. During the later Munich period he was for a time one of Baeyer's research assistants, working for a year in his private laboratory, and when he left in 1886 his position as one of the most promising of the younger chemists had become firmly established. At Munich, as at Würzburg, music was the most important of Perkin's

activities outside the laboratory. He practised assiduously on the piano, and often went to the opera.

On his return to this country Perkin was offered the use of a laboratory at Owens College, Manchester, by Professor H. B. Dixon. He worked there for a year and also filled it to overflowing with students. About the middle of this Manchester period, F. S. Kipping, who had studied at Munich in the latter part of Perkin's time there, returned to Manchester, where his people lived, and this had an important influence on Perkin's life, for at the Kipping's house he met the lady he afterwards married, who was staying at Manchester with a younger sister to whom Kipping was engaged.

In 1887 Perkin was selected from several candidates as the first Professor of Chemistry at the newly founded Heriot-Watt College at Edinburgh. He entered on his duties in October of that year, and Kipping went with him as demonstrator. Lectures at the College were all given in the evening, and this, with the daily work in the laboratories with students and on research, made term time very strenuous. A large amount of research was turned out during this period; the investigation of the synthesis of ring compounds was continued and extended; there were researches on acetylcarbinol and analogous compounds, and a large amount of work on camphor and camphoric acid (not published until later) and other subjects, but perhaps the outstanding feature was the initiation of the study of the alkaloids by the investigation of berberine and cryptopine. Perkin's brilliant researches led in 1890 to his being elected a Fellow of the Royal Society at the early age of thirty.

On the last day of 1887 Perkin married Mina, the eldest daughter of William Thomas Holland of Bridgwater. During the latter half of their time in Edinburgh the young couple lived in a house in Salisbury Road, just under Salisbury Crags, and it was there that Perkin started gardening, a hobby which he pursued with enthusiasm for the remainder of his life.

On June 27th, 1892, the Professorship of Organic Chemistry at the Owens College, Manchester, became vacant through the death of Carl Schorlemmer, and Perkin accepted the invitation of the Senate to fill the Chair. The small space available for organic students at the College was soon overcrowded, even the rooms built for research work having to be given up for the general instruction of students. On the death of Schorlemmer a fund had been raised by his old students and friends to commemorate his services to the

College and to organic chemistry, and it was generally felt that the best memorial would be a laboratory for organic chemistry to be called after his name. Perkin took an active part in planning and supervising the erection and fitting of the new laboratories, and it then became possible for him to build up a great school of research, and to enter on that exceedingly productive period which he once described as his "golden age" of research. The large Schorlemmer laboratory was filled with his students, and its reputation as a School of Research obtained world-wide recognition.

On four mornings a week Perkin lectured at 9.30, arriving at the laboratory at 8.30 on those days when he gave the general course in order to supervise his assistant's arrangement of the lecture table. These elementary lectures were profusely illustrated by experiments, and in their preparation and delivery Perkin took extreme care. They were kept fully up-to-date; his easy mode of delivery and the logical order of formulæ and other details made them almost ideal. In the advanced class his lectures covered with great clearness of treatment the more conspicuous researches on a selected group of products, and also dealt with important synthetic methods.

The rest of Perkin's day was devoted to the research students and to his own experiments. He used to go round the laboratory with unfailing regularity to see his pupils every morning. His enthusiasm was infectious and made the students feel that research work was really worth while. He was never depressed by any lack of success and was always full of encouragement. He worked at a large bench at one end of the Schorlemmer laboratory until 3·30 to 4 o'clock, with never more than an interval of half an hour for lunch at 12.30. Beginning at one end of a bench stocked with newly washed and dry apparatus (he always kept a washing boy busy), he gradually accumulated the soiled beakers and test tubes at the other end until there was little working space left and then he went home. He often worked on a very small scale, but when he had come to a decision to proceed with a synthesis or a breakdown process, a research collaborator would be asked to undertake large-scale operations involving the consumption of kilograms of initial reagents.

Between 1902 and 1904 the facilities at Manchester were increased by the addition of the "Schunck", "Dalton", and "Perkin" Laboratories (so named in honour of Sir William Perkin), but in time the increase in the number of students again led to a demand for further accommodation, which was met by the erection of the John

Morley Laboratories, opened in 1909, and there continued that ceaseless flow of research which led to the world-wide reputation of the Manchester school of organic chemistry. Investigations were carried out in this period on camphor, the terpenes, brazilin and hæmatoxylin, carbon ring compounds and bridged rings, the alkaloids, and many other subjects.

Perkin's interest in chemistry was not restricted to the organic side. He at one time preferred lecturing on inorganic chemistry, and the text-book "Inorganic Chemistry" (published in 1909), written in collaboration with Professor F. S. Kipping, became almost as standard as "Organic Chemistry" (published in 1894), written by the same authors. With Dr. Bevan Lean, Perkin collaborated in writing an "Introduction to the Study of Chemistry" (published in 1896); this, in 1901, was divided into two volumes, and was then entitled "Introduction to Chemistry and Physics". His great reputation also led to his being consulted from time to time on industrial problems, in one of which he was associated with Professor J. F. Thorpe in the development of a method of fire-proofing flannelette.

Perkin was keenly interested in cricket, and played when possible in University staff matches, making very creditable scores. He also played a very vigorous game of tennis, especially on his own lawn. His gardening in Manchester was mainly devoted to the greenhouse. He specialised in carnations, and also grew very fine chrysanthemums. He found at Manchester great scope for his musical proclivities, and from his first winter there he settled down to playing the pianoforte part in chamber music. He subscribed regularly to the Hallé Concerts, and often went to them.

In December, 1912, Perkin accepted an invitation to the Waynflete Professorship of Chemistry at Oxford, to which was attached a Fellowship at Magdalen College. From January to July, 1913, he had to carry on his work at Manchester as well as his duties at Oxford, and when his connection with Manchester University terminated in July, 1913, he had held the Professorship of Organic Chemistry for twenty-one years. It was Perkin's desire in going to Oxford to develop as rapidly as possible a school of research, and he only accepted the appointment on the understanding that the conditions would be such that he could continue his research work without any serious break. Facilities for organic chemistry at Oxford were at that time very inadequate, and while a new laboratory was being planned and built, considerable alterations were made in

the available accommodation to provide for advanced teaching and for the greatly increased number of research students.

Work on the new buildings, known as the Dyson Perrins Laboratory, was commenced in 1913, but it was delayed by the outbreak of war in 1914, and it was not until the spring of 1916 that the first section of the building was ready for occupation. It was not possible to complete the laboratory in accordance with the original plan until after the war, and it was Easter, 1922, before the second section could be opened.

Perkin brought with him from Manchester a band of assistants; they were with him for about a year, then came the war, and their dispersal. Perkin's courses of lectures at Oxford were mainly for the advanced students, or on special subjects, and as time went on he left the elementary courses more and more to his assistants. His lectures exercised a great influence; they were extraordinarily lucid and made organic chemistry a seemingly easy subject. In the laboratory he went round to the research students just as at Manchester, and this period was marked by a tremendous increase in the output of original chemical research from Oxford.

One important change which Perkin introduced at Oxford was the "Research Year" in Chemistry. The Final Examination in Chemistry in the Honour School of Natural Science was divided into two parts. Part I, taken normally at the end of a student's third year, was practically the same as the old final examination, and for Part II the candidate was required to present at the end of the next year a thesis embodying the results of experimental investigations carried out under the supervision of the University Professors or other approved persons. The Class in the examination as a whole was then awarded on the work done in both parts. He was also influential in connection with the institution of the D.Phil. degree.

The First World War involved Perkin and his department in the investigation of many problems arising out of the abnormal conditions. One noteworthy feature of this period was the establishment by British Dyes Ltd. of small colonies of chemists at various Universities. Such a colony of five to seven men was started under Perkin at Oxford. In addition to being the controller of this research team, Perkin had in 1916 accepted the post of Chairman of the Advisory Council of British Dyes Ltd. In October, 1923, he was appointed Adviser to the headquarters research staff of the British Dyestuffs Corporation (as British Dyes was now called), and

he journeyed almost weekly to Manchester to supervise the work at the research laboratories at Blackley. In March, 1924, he was made a member of the Board of Directors of the Corporation, but he ceased all active connection with it in the latter half of 1925.

During his first year or two at Oxford, Perkin threw himself energetically into the proceedings of the Men's Musical Union, of which for a time he was President, and attended the concerts regularly. He also went at times to those of the Ladies' Musical Society, and to many given by leading soloists in Oxford. Whilst in Manchester he was mainly interested in his greenhouse, but in the early Oxford days he turned to ordinary outdoor gardening, specialising in roses and herbaceous borders. He later put up a greenhouse, however, and resumed the cultivation of carnations. He greatly enjoyed his position as Fellow of Magdalen College, and had great pride in the beauty of the College. When anyone was dining with him there, he would take his guest into the cloisters or into the quadrangle to see the beautiful appearance of the buildings in the evening light or in moonlight.

Genial, large-hearted, enjoying life to the full, Perkin was enabled by his robust health to throw himself with astounding energy into whatever his hands found to do, whether it was his work or his relaxations. An excellent judge of men, he was essentially a man of action, accustomed to take swift decisions, and able to act on them. His work he loved for its own sake and was happy in it; rewards and recognition were to him of secondary importance. Perkin's home life was very happy, and his tastes were quiet. He was, however, extremely hospitable, and enjoyed entertaining those interested in the subjects he cared for. Many of the distinguished scientific and musical visitors to Manchester and to Oxford will always remember the great kindness and splendid hospitality Mrs. Perkin constantly displayed, while those whose privilege it was to know the Perkins more intimately are aware how greatly Perkin was helped by her constant sympathy with his ideals and with his work, and with what unobtrusive care she shielded him as far as possible from the minor worries and irritations of life.

In the early summer of 1929 Perkin was not well, and his indisposition became more serious as the summer went on. It was thought that a visit to Switzerland might be beneficial, and he went to his favourite hotel at Oberhofen. His condition unfortunately became worse, and it was decided that he should return home. He

bore the journey well, but there followed a rapid collapse, and he died on September 17th.

Perkin received many honours: the Longstaff Medal of the Chemical Society (1900), and the Davy Medal (1904) and Royal Medal (1925) of the Royal Society. Of the many degrees conferred on him may be mentioned Hon. M.Sc. Victoria; Hon. Sc.D. Cambridge (1910); Hon. LL.D. Edinburgh (1910); Hon. LL.D. St. Andrews (1911). He was a corresponding member of the Bavarian Academy of Science and of the Academy of Göttingen, correspondent of the Academy of Science (Institute of France), and honorary member of the Royal Society of Edinburgh, of the American Academy of Arts and Sciences, of the Belgian Academy of Medicine, and of the Royal Society of Upsala.

He served on the Council of the Royal Society during 1904—05 and 1908—10. He was a Vice-President of the Chemical Society (1906—09, 1915—23, 1924—27, 1929) and President during 1913—15.

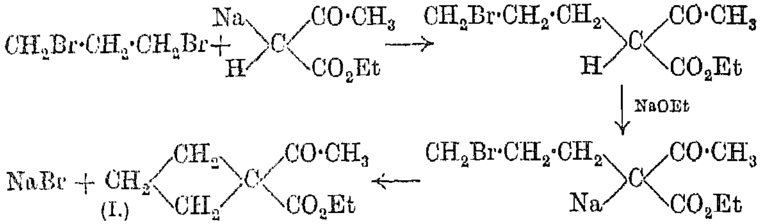
The Scientific Work of William Henry Perkin, Jun.

It is impossible in a short space to give a complete account of Perkin's contributions to organic chemical knowledge. His researches embrace many diverse fields and form the material for upwards of three hundred memoirs, mainly in the *Journal of the Chemical Society*. The following is a survey of the investigations he made in some of the more outstanding topics running through a series of papers, and many important contributions of a more miscellaneous character are omitted.

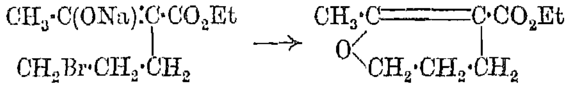
(1) *The Formation of Carbon Rings.*

Perkin in his last public lecture—the first of the Chemical Society's Pedler Lectures, delivered in 1929 (*J.*, 1929, 1347)—gave his own account of the development of his work on the synthesis of carbon rings. Every student of chemistry should read this Lecture, not only for its thrilling story of the evolution of a great idea, but also for the very interesting personal details it contains. It is unnecessary, therefore, here to give more than a brief outline of the course of these investigations. As already mentioned, Perkin embarked on this work as a young man in opposition to the prevailing views and against the advice of more experienced chemists. In his earliest experiments (*Ber.*, 1883, **16**, 208) he condensed trimethylene dibromide with the

sodium derivative of acetoacetic ester in accordance, as he thought, with the following scheme:

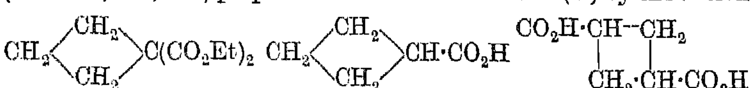


The acid obtained from the ester (I) on hydrolysis was thought to be 1-acetyl*cyclo*butane-1-carboxylic acid, in spite of the fact that it did not easily lose carbon dioxide. It was later realised by Perkin himself (*Ber.*, 1886, **19**, 1244) that the experimental observations had been misinterpreted and that the ester believed to be (I) in fact possessed the structure (II), having been formed by the alternative process:



(II.)

In the meantime Perkin had applied the above procedure to ethyl malonate (*Ber.*, 1883, **16**, 1787) and had prepared the ester (III), from which, on hydrolysis and elimination of carbon dioxide, a product giving the correct analytical data for *cyclo*butanecarboxylic acid (IV) was obtained. In this case it is clear that the dicarboxylic acid formed as the first product on hydrolysis had behaved normally, and, since the substance was different from allylacetic acid, $CH_2{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H$, its structure was beyond doubt. It is perhaps fortunate that the incorrect interpretation of the initial experiments remained undetected by Perkin's critics until irrefutable evidence in support of his views had been obtained from later work. It is of interest that Markownikoff and Krestownikoff had in 1881 (*Annalen*, **208**, 333) prepared an acid of the formula (V) by the action

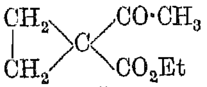
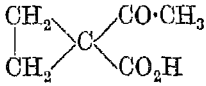
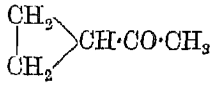


(III.) (IV.) (V.)

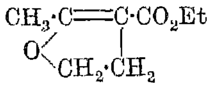
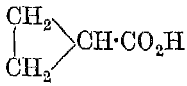
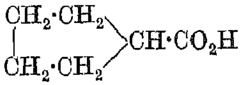
of dry sodium ethoxide on ethyl α-chloropropionate, but its structure was not completely established at the time.

The reaction between ethylene dibromide and the sodium derivative of acetoacetic ester gave a different type of product from that

obtained from trimethylene dibromide, for Perkin isolated an ester which had the properties corresponding to the structure (VI)


(VI.)

(VII.)

(VIII.)

and gave 1-acetyl*cyclo*propane-1-carboxylic acid (VII) on hydrolysis; the latter in turn readily yielded acetyl*cyclo*propane (VIII) by loss of carbon dioxide (*J.*, 1885, **47**, 829). It was shown later, however, that even in this case the oxygen ring compound (IX) is also formed, although in lesser amount (Freer and Perkin, *J.*, 1887, **51**, 820).


(IX.)

(X.)

(XI.)

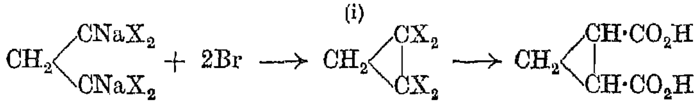
Concurrently with these experiments Perkin was investigating the action of ethylene dibromide on the sodium derivative of ethyl malonate (*Ber.*, 1884, **17**, 54), a reaction which was also being studied independently by Fittig in a different connection, and he succeeded in obtaining *cyclo*propanecarboxylic acid (X) through the corresponding intermediate compounds, although it was some years before its structure was definitely established with the preparation of the isomeric vinylacetic acid, $CH_2{:}CH{\cdot}CH_2{\cdot}CO_2H$.

From these beginnings Perkin displayed great ingenuity in developing the synthesis of numerous alicylic compounds and in overcoming obstacles. In due course difficulties in obtaining tetramethylene dibromide were surmounted (Haworth and Perkin, *J.*, 1894, **65**, 86) and the way opened for the preparation of *cyclo*pentanecarboxylic acid (XI), but in the meantime the esters,

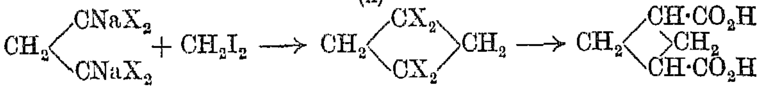
$$(CO_2Et)_2CH{\cdot}CH_2{\cdot}CH_2{\cdot}CH(CO_2Et)_2 \text{ and } (CO_2Et)_2CH{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH(CO_2Et)_2,$$

obtained as by-products from the interaction of ethylene dibromide and trimethylene dibromide respectively with the sodium derivative of ethyl malonate, were turned to advantage in various ways. A few examples of these and similar processes can be summarised in the following table taken from the Pedler Lecture ($X = CO_2Et$):

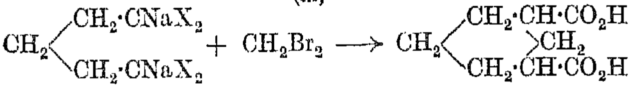
(i)



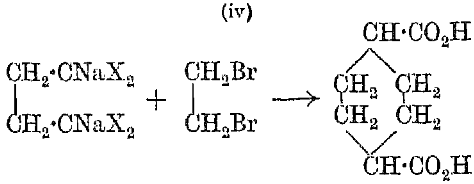
(ii)



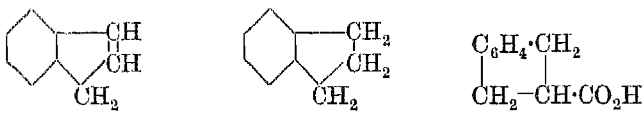
(iii)



(iv)

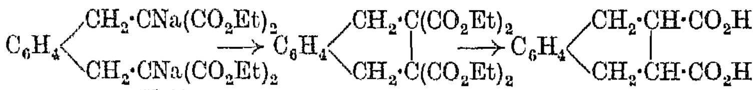


The extension of the reactions to dibromides and derivatives of malonic ester containing aromatic radicals also led to fruitful results and both indene (XII) and hydrindene (XIII) were prepared from *o*-xylylene dibromide through the acid (XIV) (Baeyer and Perkin, *Ber.*, 1884, **17**, 122; Perkin and Révay, *J.*, 1894, **65**, 228). Finally



(XII.) (XIII.) (XIV.)

a synthesis of naphthalene was accomplished by treating the sodium compound (XV) with iodine thus forming the ring compound (XVI). The distillation of the silver salt of the acid (XVII) derived from this on hydrolysis yielded naphthalene (Baeyer and Perkin, *Ber.*, 1884, **17**, 448). The ester (XVI) was also obtained from *o*-xylylene dibromide and the disodium derivative of ethanetetracarboxylic ester, $(CO_2Et)_2CH{\cdot}CH(CO_2Et)_2$.

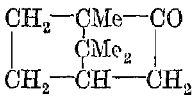


(XV.) (XVI.) (XVII.)

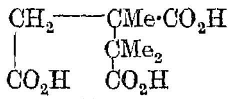
The above examples show the many-sided character of the process and the large number of derivatives of the alicyclic series which can be prepared by its means. One of the main consequences of Perkin's work in this field was Baeyer's elaboration of his " Spannungs Theorie ", a theory which has played a great part in the development of stereochemical knowledge.

(2) *The Chemistry of Camphor.*

Ordinary, natural camphor—Japan camphor—is dextrorotatory, but the lævorotatory modification occurs in *Matricaria parthenium*. Although its molecule is comparatively simple—its empirical formula is merely $C_{10}H_{16}O$—the problem of its structure proved to be exceptionally difficult and occupied the attention of a considerable number of chemists both here and abroad from 1890 and even earlier until it was finally solved and the compound prepared synthetically in 1903. Perkin and his school at Manchester took a leading part in these investigations, and it was mainly due to their efforts that the chemistry of camphor and more particularly of camphoric acid was placed upon a sure foundation. The manifold difficulties are attributable to the fact that the degradation of camphor under various conditions leads to an exceptionally large number of different products which do not seem to have any definite or direct relation either to one another or to the parent substance. As a result about thirty different formulæ for this compound have been suggested from time to time. The one now generally accepted (I) was put forward by Bredt (*Ber.*, 1893, **26**, 3047), and was in the first instance largely based upon the behaviour of camphoronic acid, $C_9H_{14}O_6$, one of the substances obtained by the oxidation of camphor. This acid was found to be tribasic, and, when subjected to heat, gave trimethylsuccinic acid, *iso*butyric acid, and free carbon. Bredt therefore gave it the formula (II), and owing to the close



(I.)



(II.)

connection of this acid with camphor itself it became a matter of great importance to confirm its structure by synthesis. This was accomplished by Perkin and Thorpe (*J.*, 1897, **71**, 1169) by taking advantage of the reaction just previously introduced by Reformatsky whereby ketones are condensed with halogen derivatives of esters through the agency of zinc in accordance with the general scheme :

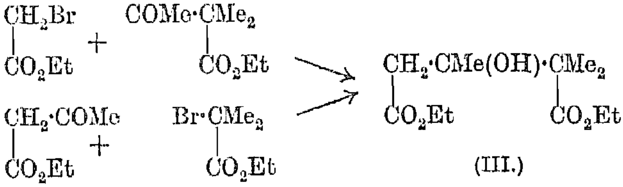
$$>CO + CH_2BrX \xrightarrow{Zn} >C(OZnBr)\cdot CH_2X$$

$$\downarrow HCl$$

$$>C(OH)\cdot CH_2X + ZnClBr$$

The hydroxy-ester (III) was obtained by two alternative routes. In

one of these bromoacetic ester was condensed with the dimethyl derivative of acetoacetic ester, and in the other α-bromo*iso*butyric ester with acetoacetic ester itself:



(III.)

It then remained merely to follow the usual procedure OH ⟶ Br ⟶ CN ⟶ CO_2H in order to synthesise camphoronic acid, but considerable difficulties were encountered in these later stages. The substitution of Br for OH was comparatively easy, but treatment of the bromo-ester with the strongly alkaline potassium cyanide of those days led mainly to trimethylglutaconic acid,

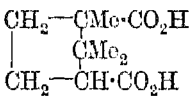
$$CO_2H\cdot CH{:}CMe\cdot CMe_2\cdot CO_2H.$$

Fortunately camphoronic acid gives a characteristic calcium salt which only separates from a boiling solution and it was possible to isolate by this means the relatively small amount of that acid formed in accordance with the original design, and thereby to prove its structure.

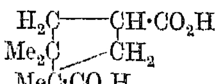
Meanwhile Perkin was looking for new degradation products from which fresh light on the constitution of camphor and camphoric acid, another of its important oxidation products, might be obtained. He chose as his starting point sulphocamphylic acid, obtained by the action of concentrated sulphuric acid on camphoric acid—a change represented empirically as follows:

$$C_{10}H_{16}O_4 + H_2SO_4 = C_9H_{14}O_5S + CO + 2H_2O.$$

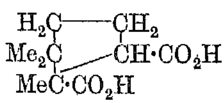
As a result of this work Perkin was led to depart from the Bredt formula for camphoric acid (IV) and to propose two other formulæ, (V) and (VI), of which he preferred the former. When sulpho-



(IV.)



(V.)



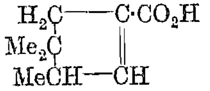
(VI.)

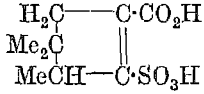
camphylic acid is heated it passes into sulphuric acid and *iso*-lauronolic acid, thus,

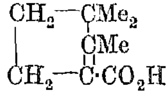
$$C_8H_{12}(SO_3H)\cdot CO_2H,H_2O \longrightarrow C_8H_{13}\cdot CO_2H + H_2SO_4$$

and from the fact that *iso*lauronolic acid on oxidation with the

calculated quantity of alkaline permanganate yields acetyldimethylbutyric acid, $MeCO{\cdot}CMe_2{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H$, he represented it as having the structure (VII) and sulphocamphylic acid (VIII). As we now know, *iso*lauronolic acid has the formula (IX) and it is

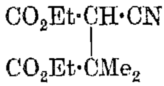

(VII.)

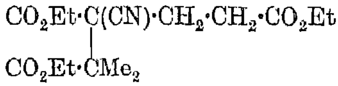

(VIII.)

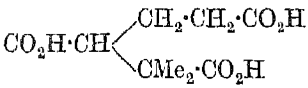

(IX.)

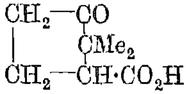
doubtful whether Perkin ever regarded his structural views as having more than a tentative character.

The Bredt formula continued to be pre-eminent during this period, and under its stimulus the first synthesis of *i*-camphoric acid was accomplished in 1903 (Perkin and Thorpe, *Proc.*, 1903, **19**, 61; *J.*, 1904, **85**, 128). The condensation of ethyl sodiocyanoacetate with ethyl α-bromo*iso*butyrate gave the ester (X), from the sodium derivative of which the compound (XI) was obtained by further reaction with ethyl β-iodopropionate. Hydrolysis and elimination of carbon dioxide then led to the acid (XII). A new reaction was introduced here, for, instead of the wasteful method of calcium salt distillation being used, it was found that the ketone (XIII) could be

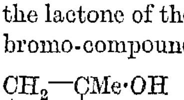

(X.)

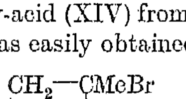

(XI.)

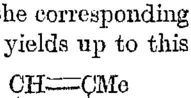

(XII.)


(XIII.)

obtained by the action of acetic anhydride on the sodium salt of the acid. The usual reaction with methylmagnesium iodide then gave the lactone of the hydroxy-acid (XIV) from which the corresponding bromo-compound (XV) was easily obtained. The yields up to this


(XIV.)


(XV.)


(XVI.)

point were excellent, but trouble arose in the reaction Br $\longrightarrow$ CN $\longrightarrow$ CO_2H, just as in the previous synthesis of camphoronic acid. The difficulty here was enhanced because no friendly calcium salt could be produced, and the α-campholytic acid (XVI) formed by loss of

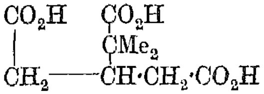
hydrogen bromide showed a marked tendency to pass over into *iso*lauronolic acid (IX). Large quantities of material were used and every device that could be thought of was employed in order to prevent the elimination of hydrogen bromide during the introduction of the nitrile group, but without any great measure of success. Nevertheless enough *i*-camphoric acid was obtained for identification, although not, at that stage, for analysis, and the correctness of the Bredt formula was established. Subsequently the work was repeated (Perkin and Thorpe, *J.*, 1906, **89**, 795) and quite a large quantity of *i*-camphoric acid prepared. Meanwhile Komppa had published his synthesis of camphoric acid from ββ-dimethylglutaric acid (*Ber.*, 1903, **36**, 4332), a route which undoubtedly constituted a better method for its preparation on a considerable scale.

In all his main researches Perkin had a number of auxiliary investigations in progress, which not only helped him directly but have proved of inestimable value to many workers in other fields. Thus in connection with camphor he realised that a study of the derivatives of glutaric and succinic acids was essential to the work he had in hand. In some of these investigations use was made of the Michael reaction, and our knowledge of this important synthetic agency was thereby greatly increased. One of these researches resulted in the synthesis of αββ-trimethylglutaric acid,

$$CO_2H{\cdot}CHMe{\cdot}CMe_2{\cdot}CH_2{\cdot}CO_2H,$$

by treating ethyl dimethylacrylate, $CO_2Et{\cdot}CH{:}CMe_2$, with ethyl sodiocyanoacetate, and then acting on the sodium compound, formed in the condensation, *in situ* with methyl iodide (Perkin and Thorpe, *J.*, 1899, **75**, 61). The synthesis of this acid was important because Balbiano had obtained it by the reduction of an acid, $C_8H_{12}O_5$, which he had prepared from camphoric acid by oxidation with cold permanganate. Another investigation concerned the structure of *iso*camphoronic acid—one of the most vexing problems of the period. This acid is not only an oxidation product of α-campholenic acid, which can be prepared by the dehydration of camphoroxime, and the hydrolysis of the nitrile so formed, but is also produced in the oxidation of pinene. Tiemann regarded it as having the structure (XVII), but Baeyer in view of its formation from pinene favoured the formula (XVIII). The latter structure was eliminated by its synthesis from the sodium compound formed in the condensation of ethyl dimethylacrylate with ethyl sodiocyanoacetate. After this had been further condensed *in situ* with ethyl bromoacetate, the corresponding tribasic acid, differing from

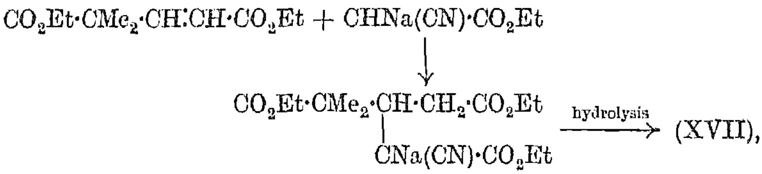
*iso*camphoronic acid, was obtained on hydrolysis (Perkin and



$CO_2H{\cdot}CH_2{\cdot}CMe_2{\cdot}CH(CO_2H){\cdot}CH_2{\cdot}CO_2H$

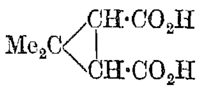
(XVII.) (XVIII.)

Thorpe, *J.*, 1899, **75**, 897). *iso*Camphoronic acid was then prepared by Perkin in accordance with the following scheme :

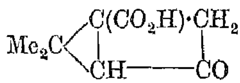


and the correctness of Tiemann's formula established (*J.*, 1902, **81**, 246).

The introduction of ethyl cyanoacetate in place of ethyl malonate in the Michael reaction led to such increased yields that acids such as ββ-dimethylglutaric acid (from cyanoacetic ester and dimethylacrylic ester) were available for use in large quantities. Further researches with ββ-dimethylglutaric acid led to the synthesis of both the *cis*- and the *trans*-form of caronic acid (XIX) (Perkin and Thorpe, *J.*, 1899, **75**, 48), of importance in connection with the structure of carene, and to the preparation of the dicyclic compound (XX) (Perkin and Thorpe, *J.*, 1901, **79**, 729), a substance of considerable interest from the fact that it exhibits intra-annular tautomerism.

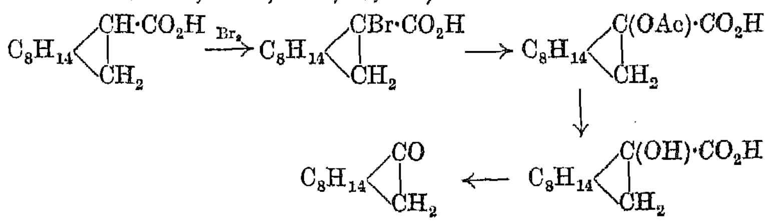


(XIX.)

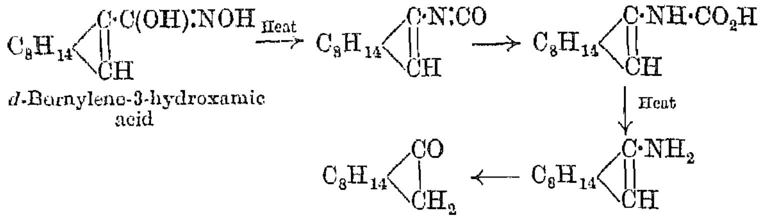


(XX.)

Perkin later studied the preparation and properties of *epi*camphor —that is, camphor in which the position of the $CH_2{\cdot}CO$ group is reversed. A small amount of this substance was obtained from *d*-camphane-3-carboxylic acid as in the following scheme (Lankshear and Perkin, *Proc.*, 1911, **27**, 166) :



but the method was not very good. Meanwhile Bredt at about the same time (*Chem. Zeit.*, 1911, **35** 765) had employed a different process which was also unsuitable for use on a large scale, and the two chemists then collaborated in the development of the following method (Bredt and Perkin, *J.*, 1913, **103**, 2182), which was found to give highly satisfactory results :



d-Bornylene-3-hydroxamic acid

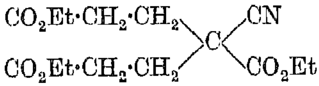
The very violent character of the pyrogenetic decompositions involved can be overcome by using the acetyl or benzoyl derivative of bornylenehydroxamic acid.

(3) *The Chemistry of the Terpenes.*

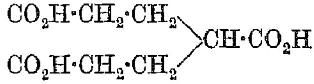
The chemical nature of the terpenes, which are hydrocarbons found widely distributed in the essential oils of plants, excited a great deal of interest in the closing years of the nineteenth century. The laborious researches of Wallach, Baeyer, and many others, and the brilliant theoretical deductions of Wagner, had gone far towards establishing the structural formulæ of the more important of these natural products and their numerous derivatives, but the evidence was derived from degradative transformations, and it was clear to Perkin that the synthetical preparation of some of the key substances was essential in order to remove many doubts and eliminate rival formulæ. Limitations of space preclude any account of the situation in this intricate field at the time Perkin embarked on his experiments, and make it impossible, therefore, to indicate the full significance of his syntheses. Reference can only be made to a few of the more outstanding features of researches which contributed so much towards placing the structure of the terpenes on a sure foundation.

Limonene (dipentene) occurs extensively not only in both its optically active modifications but also in the *dl*-form, and many problems of terpene chemistry are linked with the structure of this substance and the closely related compounds, terpineol and terpin. Perkin (*J.*, 1904, **85**, 654) condensed ethyl β-iodopropionate with ethyl cyanoacetate in two stages through the sodium derivatives

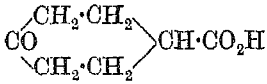
to obtain the ester (I) which was converted to the acid (II) by hydro-



(I.)

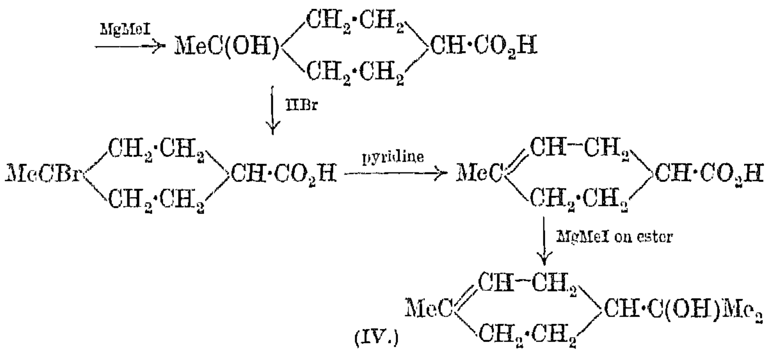


(II.)



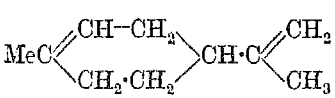
(III.)

lysis with hydrochloric acid. The keto-acid (III) was prepared from this tribasic acid by heating its sodium salt with acetic anhydride, and the following series of reactions then led from the corresponding ester to *i*-terpineol (IV):

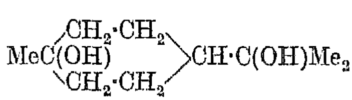


(IV.)

Perkin converted *i*-terpineol to *i*-dipentene (V) by heating with potassium hydrogen sulphate, and to terpin (VI) by shaking with dilute sulphuric acid, and so confirmed the structural formulæ advanced for these substances by Wagner in 1894.



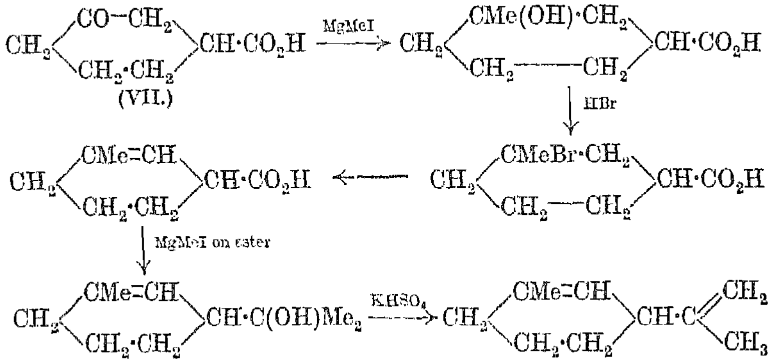
(V.)



(VI.)

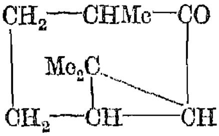
A similar series of reactions starting from the ester of *cyclo*-hexanone-3-carboxylic acid (VII) led to the important substance carvestrene (VIII) (Perkin and Tattersall, *J.*, 1907, **91**, 480). Carvestrene, which was obtained by Baeyer from carvone by an interesting series of transformations through carone, is *dl*-sylvestrene, and *d*-sylvestrene is found in Swedish oil of turpentine. Many

synthetic terpenes have been prepared by Perkin and his collaborators from keto-acids of the type here illustrated. Obviously the

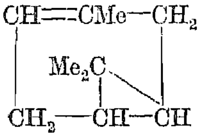


(VII.) (VIII.)

method is capable of wide application and the number of terpene-like substances that can be prepared by its aid is very large. In these synthetical processes extensive use was made of the reactions with methylmagnesium iodide just previously developed by Grignard.



(IX.)



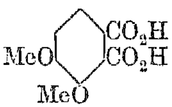
(X.)

Reference has been made in the previous section to Perkin's synthesis of caronic acid, obtained earlier by Baeyer by the oxidation of carone (IX) with permanganate. This acid was later obtained by the oxidation of carene (X), isolated by Simonsen from *Pinus longifolia*, and so played an important part in establishing the constitution of the terpene.

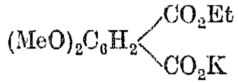
(4) *The Constitution of Berberine.*

No doubt Perkin's interest in the complex natural bases was stimulated by his association with Königs in Baeyer's laboratory at a time when alkaloids were very much in the air. Nevertheless, the determination to unravel the molecular structure of berberine was a courageous one for a young chemist of that time. This alkaloid was discovered in 1826, and, after some erroneous work by other

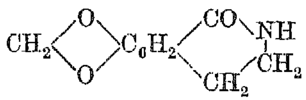
authors, J. Dyson Perrins (1861, 1862) established the composition of the base which is now accepted, although, strictly speaking, this formula, $C_{20}H_{17}O_4N$, is derived from the ascertained composition of salts presumed to be of the type B,HX. We now know that the chloride, $C_{20}H_{18}O_4NCl$, is actually related to a base $C_{20}H_{19}O_5N$ of ammonium hydroxide type. Impressed by the results obtained by Goldschmiedt during the oxidation of papaverine, Perkin, in his Edinburgh days, carried out a careful investigation of the action of potassium permanganate on berberine (*J.*, 1889, **55**, 63; 1890, **57**, 992). There were isolated hemipinic acid ($C_{10}H_{10}O_6$), hemipinic anhydride ($C_{10}H_8O_5$), ω-aminoethylpiperonylcarboxylic anhydride ($C_{10}H_9O_3N$), hydrastic acid ($C_9H_6O_6$), anhydroberberilic acid ($C_{20}H_{17}O_8N$), berberilic acid ($C_{20}H_{19}O_9N$), berberal ($C_{20}H_{17}O_7N$), berilic acid ($C_{20}H_{15}O_8N$), oxyberberine ($C_{20}H_{17}O_5N$), and dioxyberberine ($C_{20}H_{17}O_6N$). Perkin's remarkable laboratory technique is well illustrated by the separation and characterisation of these products. He took great pains to identify the hemipinic acid (I) produced in the oxidation; the formation of hemipinic anhydride was unexpected and, at that time, the conversion into a potassium ethyl hemipinate (II) by means of alcoholic potash was even more surprising.



(I.)



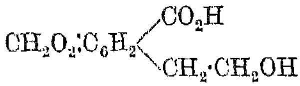
(II.)

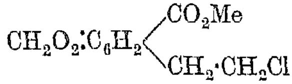


(III.)

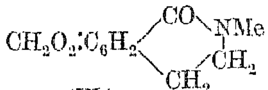
The central position in the research was occupied by the substance $C_{10}H_9O_3N$, which was identified as ω-aminoethylpiperonylcarboxylic anhydride (III). Although, at a later stage, hydrastic acid, $CH_2O_2{:}C_6H_2(CO_2H)_2$, was isolated from the oxidation products of berberine, the feebly basic substance $C_{10}H_9O_3N$ was independently recognised as a piperonyl derivative. Its relation to Freund's oxyhydrastinine was early suspected and an important stage of the investigation was completed when Perkin succeeded in establishing this by a direct conversion of the one substance into the other. The anhydride, $C_{10}H_9O_3N$, yielded a yellow *N*-nitroso-derivative, and this was decomposed by hot aqueous sodium hydroxide with formation of a salt of an acid, $C_{10}H_{10}O_5$ (IV). The latter also yielded an anhydride (lactone) and the action of phosphorus pentachloride and subsequent esterification then furnished the chloro-ester (V). This ester was nearly quantitatively transformed by methylamine

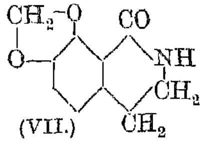
into oxyhydrastinine (VI) identical with the substance derived from hydrastine and already investigated by Freund and Will. Although


(IV.)

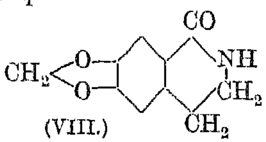

(V.)

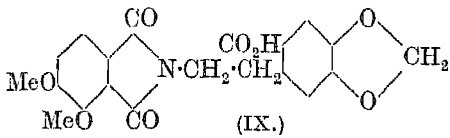
well aware that evidence on the point was lacking, Perkin unfortunately misplaced the methylenedioxy-group in the benzene ring


(VI.)


(VII.)

and adopted the formula (VII) for the anhydride $C_{10}H_9O_3N$ and other formulæ to correspond. This was formally corrected in 1910, but the relation of hydrastic acid to metahemipinic acid was known long before this, so the correction was hardly necessary. The formula (VIII) for the anhydride $C_{10}H_9O_3N$ will therefore be employed in the sequel.

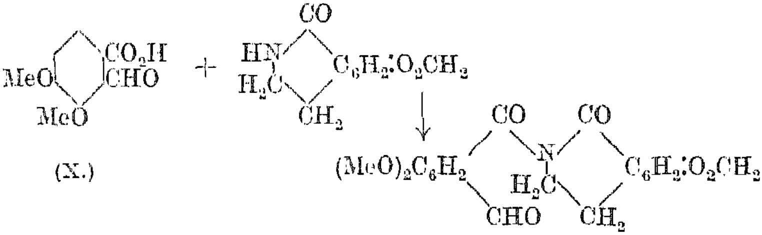

(VIII.)


(IX.)

One of the chief products of the permanganate oxidation was an acid, $C_{20}H_{17}O_8N$, termed anhydroberberilic acid, readily convertible by aqueous potassium hydroxide into berberilic acid, $C_{20}H_{19}O_9N$. These acids are formed from berberine without loss of carbon, and hence it was of importance to gain an insight into their structure. Hydrolytic fission of berberilic acid, by means of dilute sulphuric acid, afforded hemipinic acid and ω-aminoethylpiperonylcarboxylic acid. Furthermore, the synthesis of anhydroberberilic acid (IX) was effected by heating the hemipinate of aminoethylpiperonylcarboxylic acid.

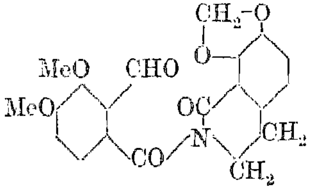
Even more interesting results followed from the study of berberal, $C_{20}H_{17}O_7N$. On treatment with boiling alcoholic potash or boiling dilute sulphuric acid, this neutral substance was degraded to pseudopianic acid, which was shown to have the structure (X), and the anhydride, $C_{10}H_9O_3N$ (VIII). Again, by simply heating these substances together, berberal was regenerated, and it seemed

obvious at the time that the process should be formulated according to the scheme :

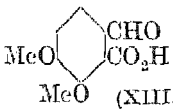


(X.)

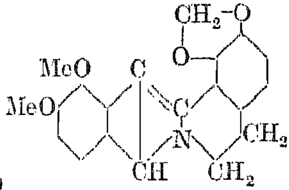
Thus the formula (XI) was assigned to berberal in 1890 by Perkin, and this led to the formula (XII) for berberine itself. Reference to the correction of the position of the methylenedioxy-group has been already made and two further changes in the expression (XII) were found to be necessary.



(XI.)

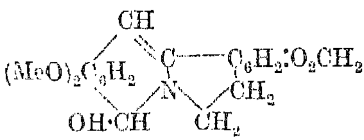


(XIII.)

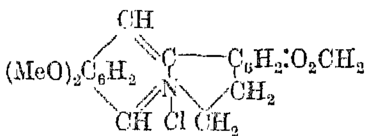


(XII.)

It gradually became clear that the base berberine, $C_{20}H_{17}O_4N$, has only a hypothetical existence and that the substance precipitated by the action of alkalis on a berberine salt solution is in reality a carbinol-base of the formula $C_{20}H_{19}O_5N$. This, as especially Tinkler (*J.*, 1911, 99, 1340) has shown by a spectrometric method, is in equilibrium with an ammonium hydroxide form, *berberinium hydroxide*. The carbinol may be termed *berberinol*, but Perkin has suggested that the older name, *berberine*, should be retained with the new significance.

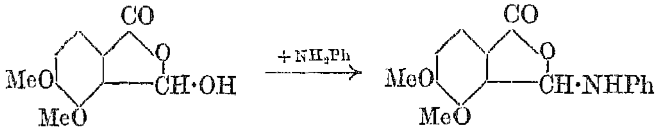


Berberinol or berberine.

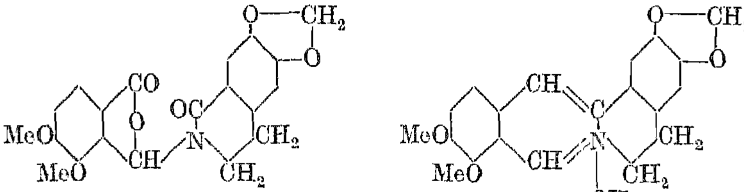


Berberinium chloride.

Then in 1910 (Perkin and Robinson, *J.*, 1910, 97, 305) a change in the position of the methoxy-groups in (XII) was proposed for two reasons. In the first place it was observed that hydrastine and berberine occur together in *Hydrastis canadensis* and therefore the orientation of the methoxyl groups is likely to be the same in the two alkaloids. In the second place, studies of the course of the condensations of opianic acid (XIII) with a large variety of substances (alcohols, amines, aromatic nuclei) had made it probable that the earlier formulation of the berberal synthesis was open to question and the position of the methoxyls was fixed solely as a result of this interpretation. Thus Liebermann (*Ber.*, 1886, 19, 2284; 1896, 29, 175) considered that the facile condensation of opianic acid with aniline occurred in the following manner:



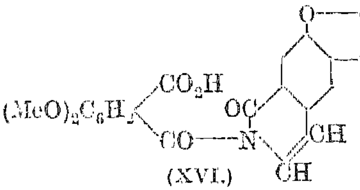
Therefore the constitution (XIV) was proposed for berberal and (XV) for berberinium hydroxide. Obvious modifications of (XV) are the carbinol [-CH(OH)-N:] and the open-chain aldehyde, berberinal (-CHO NH:).



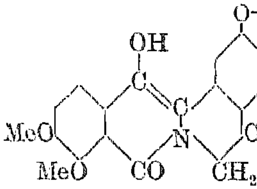
(XIV.) (XV.)

The other products of the permanganate oxidation of berberine isolated by Perkin were not very closely studied by him at the time. Berilic acid was obtained in very small yield, and it is probable that this is now best formulated by (XVI). The neutral compound dioxyberberine, $C_{20}H_{17}O_6N$, has the formula (XVII), and it is of interest that this substance absorbs oxygen in methyl-alcoholic potash and is converted into berberilic acid. But the most important of the neutral products of the oxidation was oxyberberine, $C_{20}H_{17}O_5N$, considered by Perkin to be the primary product of the oxidation and now represented by (XVIII).

Gadamer (*Arch. Pharm.*, 1905, **243**, 35; compare Faltis, *Monatsh.*, 1910, **31**, 557, and Gadamer, *Arch. Pharm.*, 1910, **248**, 670) was the first to show that berberine is converted by aqueous sodium hydroxide on the steam-bath into oxyberberine and dihydroanhydroberberine (XIX) by a Cannizzaro-type reaction. Perkin (*J.*, 1918,

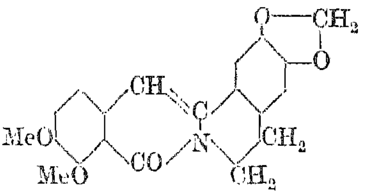


(XVI.)

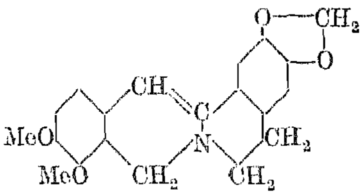


(XVII.)

113, 764) reduced oxyberberine electrolytically to the known tetrahydroanhydroberberine (formerly tetrahydroberberine), which can readily be oxidised by iodine to berberinium iodide. This completed a synthesis of berberine due to Pictet and Gams (*Compt. rend.*, 1911, **152**, 1102; **153**, 386; *Ber.*, 1911, **44**, 2036), who claimed to have



(XVIII.)



(XIX.)

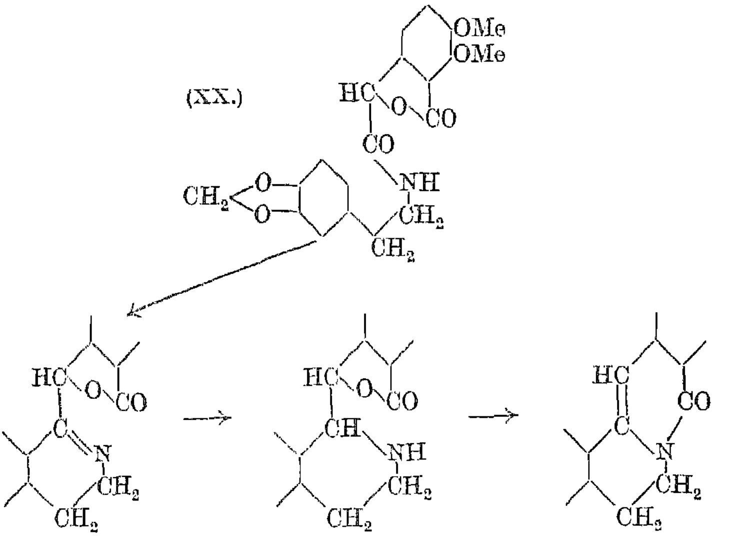
obtained oxyberberine by a series of processes. However, this synthesis and also that of tetrahydroberberine by the same chemists (*loc. cit.*) have been subjected to severe criticism, and the validity of these investigations as proofs of structure by synthesis has been questioned.

Two independent syntheses of oxyberberine were therefore made by Perkin and his co-workers. In the first (Perkin, Rây, and Robinson, *J.*, 1925, **127**, 740) the β-piperonylethylamide (XX) of meconinecarboxylic acid was dehydrated by means of phosphoryl chloride; the product furnished oxyberberine on reduction with zinc and acetic acid. The process is illustrated in the scheme on page 200.

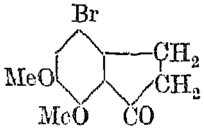
The second method (Haworth, Koepfli, and Perkin, *J.*, 1927, 548) had been previously applied by Perkin to other cases. β-Veratrylpropionic acid was brominated and dehydrated to the bromodi-

methoxyindanone (XXI), the *iso*nitroso-derivative of which reacted with *p*-toluenesulphonyl chloride in alkaline solution with the

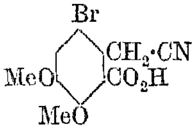
(XX.)



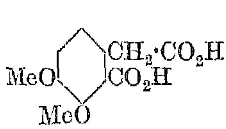
formation of the nitrile (XXII). Hydrolysis and reduction then afforded a dimethoxyhomophthalic acid (XXIII). The action of



(XXI.)

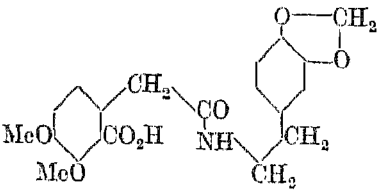


(XXII.)

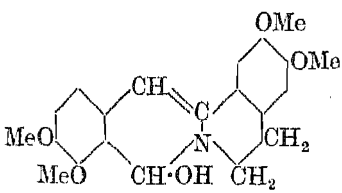


(XXIII.)

the anhydride of this acid on β-piperonylethylamine gave the phthalamic acid (XXIV), the methyl ester of which was converted into oxyberberine by means of boiling phosphoryl chloride. In a similar manner the synthesis of palmatine (XXV) was effected through oxypalmatine and tetrahydroanhydropalmatine.



(XXIV.)

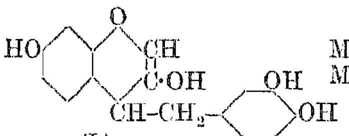


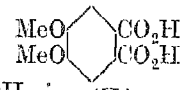
(XXV.)

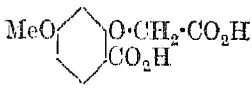
(5) *Brazilin and Hæmatoxylin.*

Although experiments on brazilin and hæmatoxylin were initiated by Perkin in 1883 the first publications did not appear until some sixteen years later. Brazilin, $C_{16}H_{14}O_5$, and hæmatoxylin, $C_{16}H_{14}O_6$, are very closely related, the latter being a hydroxy-derivative of the former, and brazilin alone will be dealt with in the first place. This substance is the colouring matter of Brazil-wood, and its composition was first accurately determined by Liebermann and Burg (*Ber.*, 1876, **9**, 1883), who also showed that it contained four hydroxyl groups. That three of these are phenolic was subsequently established by Dralle (*Ber.*, 1884, **17**, 375), and sufficient progress had been made with its study by several different workers for Feuerstein and Kostanecki to be able to suggest the formula (I) for the substance by the end of last century (*Ber.*, 1899, **32**, 1025).

In one series of experiments Perkin attacked the problem of the structure of brazilin along lines similar to those which had proved so successful in the case of berberine—that is, by the action of potassium permanganate on trimethylbrazilin, in which the phenolic hydroxyl groups were protected by methylation (Gilbody, Perkin, and Yates, *J.*, 1901, **79**, 1396; Perkin, *J.*, 1902, **81**, 221, 1008). The products were brazilinic acid, $C_{19}H_{18}O_9$; brazilic acid, $C_{12}H_{12}O_6$; an acid, $C_{10}H_{10}O_6$, m. p. 174°; an acid, $C_{10}H_{10}O_6$, m. p. 195°; an acid, $C_{11}H_{12}O_6$; an acid, $C_{11}H_{10}O_7,2H_2O$; an acid, $C_{11}H_{10}O_7$, m. p. 216°; and acetic, formic, and oxalic acids. The acid $C_{10}H_{10}O_6$, m. p. 195°, was identified as *m*-hemipinic acid (II), and this disproved at once the brazilin formulation of Feuerstein and Kostanecki. The


(I.)

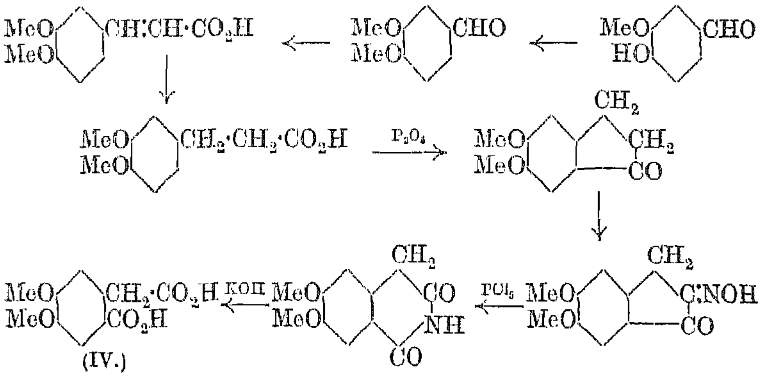

(II.)


(III.)

acid $C_{10}H_{10}O_6$, m. p. 174°, was found by potash fusion to be a derivative of resorcinol; it was proved to be dibasic ($C_{10}H_8O_6Ag_2$) and when heated with water at 200° it yielded a monobasic acid, $C_7H_6O(OMe)(CO_2H)$. This was synthesised by hydrolysis of the ester produced by the condensation of the sodium derivative of resorcinol monomethyl ether and ethyl bromoacetate. The monobasic acid was therefore *m*-methoxyphenoxyacetic acid and, the frequent formation of resorcylic acid derivatives from brazilin being

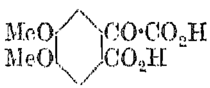
taken into consideration, the acid $C_{10}H_{10}O_6$ was recognised as 2-carboxy-5-methoxyphenoxyacetic acid (III). The synthesis of this acid (Perkin and Robinson, *J.*, 1908, 93, 489) was effected by introducing the group $CH_2 \cdot CO_2H$ into *p*-methoxysalicylaldehyde, followed by oxidation of the product.

The acid $C_{11}H_{12}O_6$ was found to be dibasic and a derivative of catechol; in composition it is a homologue of *m*-hemipinic acid, and therefore the formula (IV) was suggested for it. This was proved to be correct by a synthesis (Perkin and Robinson, *J.*, 1907, 91, 1073) in the stages:

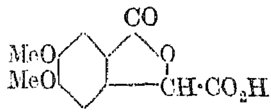


(IV.)

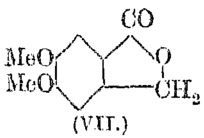
Similarly the dibasic acid $C_{11}H_{10}O_7,2H_2O$ was also found to be a catechol derivative, and from its composition the formula (V) was indicated. In harmony with this view the acid was reduced by sodium amalgam to a dimethoxyphthalidecarboxylic acid (VI), which when heated furnished *m*-meconine (VII). The constitution of the acid $C_{11}H_{10}O_7$, m. p. 216°, obtained in minute relative amount was never competely cleared up.



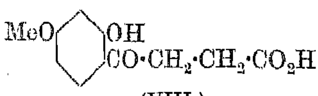
(V.)



(VI.)



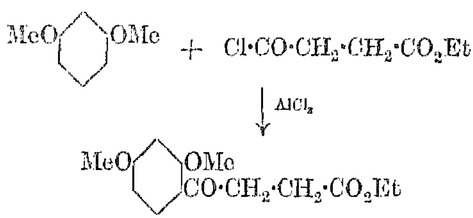
(VII.)



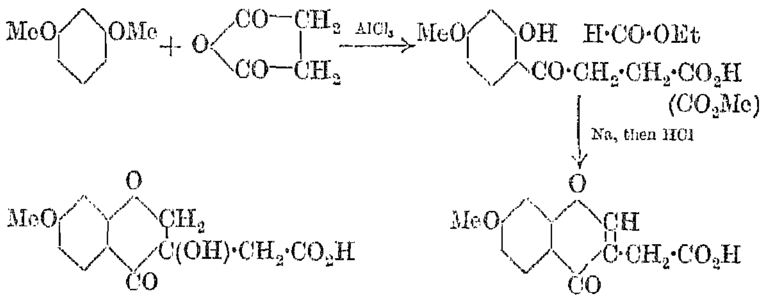
(VIII.)

The two most important oxidation products were brazilic acid

and brazilinic acid. The former, a monobasic acid, was found to be a derivative of resorcinol and furnished a semicarbazone and oxime; on reduction a dihydrobrazilic acid was formed, and this gave a lactone. The action of sulphuric acid produced anhydrobrazilic acid, $C_{12}H_{10}O_5$, and on hydrolysis by means of boiling baryta solution this derivative afforded formic acid and an acid $C_{11}H_{12}O_5$; the latter gave a violet coloration with ferric chloride and a methyl ether, $C_{12}H_{14}O_5$, which was still a carboxylic acid and contained two methyl groups. The nature of these acids could be deduced to a large extent from the known facts, and the synthesis of the acid $C_{12}H_{14}O_5$ was effected by treating a mixture of resorcinol dimethyl ether and the ester of the half-chloride of succinic acid with aluminium chloride and hydrolysing the product:



Taking cognisance of the oxidation of anhydrobrazilic acid to *p*-methoxysalicylic acid, it was evident that the acid $C_{11}H_{12}O_5$ must have the formula (VIII). Its relation to anhydrobrazilic acid (IX) was considered to be analogous to that of fisetol to fisetin, and a synthesis of anhydrobrazilic acid justified the argument:

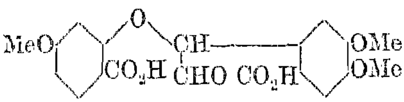


(X.) (IX.)

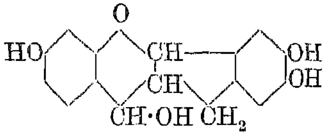
The constitution of brazilic acid itself was then clearly (X), partly because the acid did not yield a lactone (and yet its dihydro-derivative would do so), and partly in view of the simultaneous formation

of other acids (III and IV) with the methylene groups of the formula (X), in the oxidation of trimethylbrazilin.

Brazilinic acid was the sole product of the reaction which retained all the carbon atoms of the brazilin molecule. It was shown to be a dibasic acid containing a carbonyl group. On reduction with sodium amalgam it gave a hydroxy-acid, not isolated, which passed over to the lactone of dihydrobrazilinic acid. Perkin proposed the formula (XI) for brazilinic acid and the formula (XII) for brazilin itself. He was nevertheless unable to oxidise brazilinic acid to a tribasic acid, $C_{19}H_{18}O_{10}$, and moreover the formula (XII) does not contain the group $\cdot O \cdot CH_2 \cdot C$, which occurs in brazilic acid and carb-

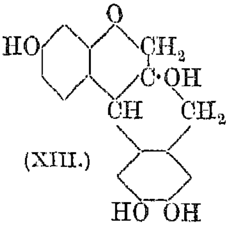


(XI.)

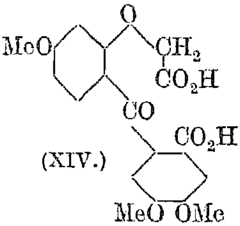


(XII.)

oxymethoxyphenoxyacetic acid (III). The most likely alternative to (XII) was the formula (XIII), which had already been suggested by Werner and Pfeiffer (*Chem. Zeitsch.*, 1904, **3**, 421), and from 1907 this formula, which was gradually proved to be correct, was used as a working hypothesis.



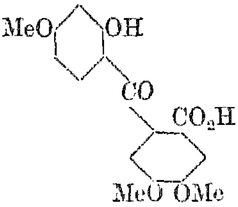
(XIII.)

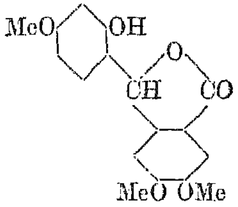


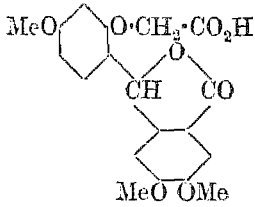
(XIV.)

On the basis of the formula (XIII), brazilinic acid should be represented by the expression (XIV), and the synthesis was effected (Perkin and Robinson, *J.*, 1908, **93**, 489) by treating a mixture of ethyl *m*-methoxyphenoxyacetate and *m*-hemipinic anhydride with aluminium chloride. The yield was poor, and a better synthesis of the lactone of dihydrobrazilinic acid was discovered. Resorcinol dimethyl ether and *m*-hemipinic anhydride with aluminium chloride under rather vigorous conditions furnished the hydroxymethoxybenzoylveratric acid (XV), which was reduced to a lactone (XVI). The

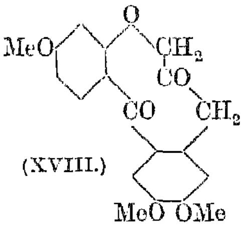
action of sodium chloroacetate on the sodium derivative of (XVI) gave the required lactone of dihydrobrazilinic acid (XVII).

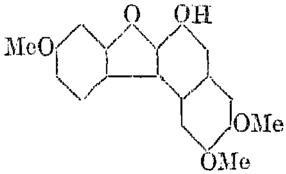

(XV.)

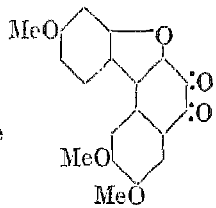

(XVI.)


(XVII.)

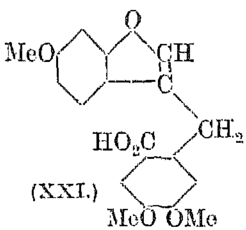
The oxidation of trimethylbrazilin with chromic acid gave a crystalline compound termed trimethylbrazilone, the accepted formula of which (XVIII) was finally advanced in 1927. Dehydrating agents converted trimethylbrazilone into the β-naphthol derivative (XIX), and when the product obtained from the substance (XVIII) by successive treatment with acetic anhydride and nitric acid was

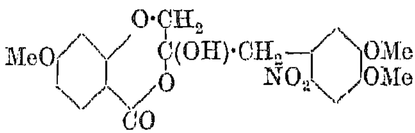

(XVIII.)


(XIX.)


(XX.)

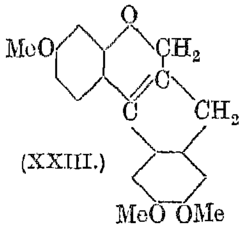
hydrolysed, reduced, and then oxidised, an *o*-quinone termed trimethoxy-α-brazanquinone (XX), was obtained. The action of concentrated sulphuric acid led to a coumarone derivative (XXI),


(XXI.)

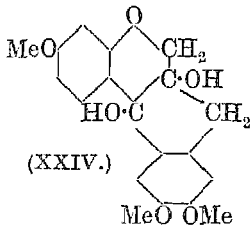

(XXII.)

which in turn exhibited a complex series of transformations under various conditions. Concentrated nitric acid reacted with trimethylbrazilone to give a compound (XXII), the reactions of which were also closely studied. When reduced with phenylhydrazine,

trimethylbrazilone gave deoxytrimethylbrazilone (XXIIII), while the use of zinc dust in alcoholic acetic acid solution furnished the pinacol (XXIV). The compound (XXIII) was synthesised at a later

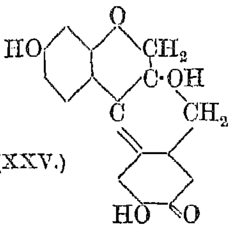


(XXIII.)

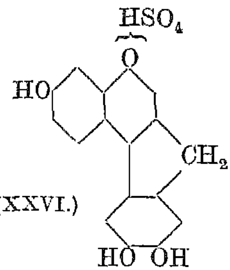


(XXIV.)

date, but it is impossible here to describe in detail the complex chemistry of the trimethylbrazilone derivatives and the part they played in the development of the brazilin formula.

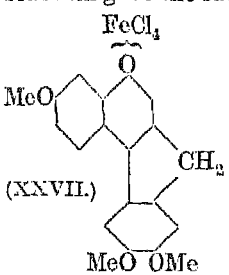


(XXV.)

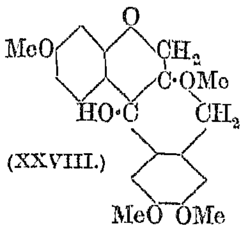


(XXVI.)

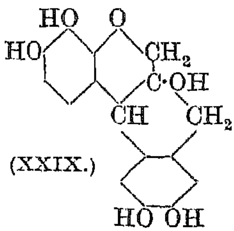
Another extensive series of investigations embraced the derivatives of brazilein, $C_{16}H_{12}O_5$, obtained when brazilin is oxidised under a variety of mild conditions. The formula (XXV) was ultimately advanced for brazilein, and one of the most striking properties of this substance, its methyl derivatives, and certain related compounds, is the conversion into indenobenzopyrylium salts by means of mineral acids. Thus the action of sulphuric acid on brazilein gave the salt (XXVI), while the ferrichloride (XXVII) was



(XXVII.)

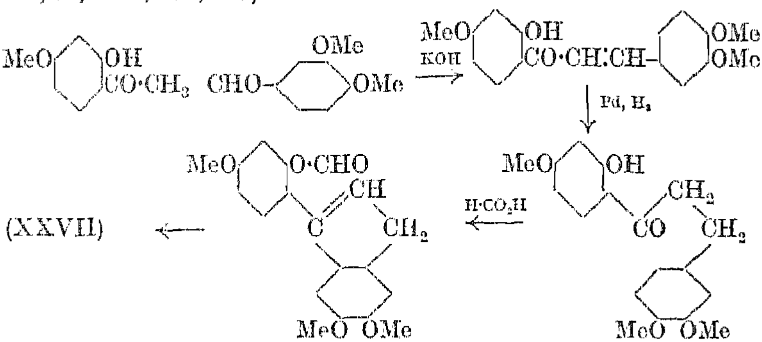


(XXVIII.)



(XXIX.)

derived from tetramethyldihydrobrazileinol (XXVIII), which was obtained by the further methylation of the substance formed when trimethylbrazilein was dissolved in boiling aqueous potassium hydroxide. Some of these salts were synthesised by an application of reactions now well known in the benzopyrylium series. The ferrichloride (XXVII) was obtained by heating the ketone (XXX) with anhydrous formic acid and zinc chloride and treating the product with hydrochloric acid and ferric chloride (Crabtree and Robinson, *J.*, 1918, *113*, 859).



Hypothetical intermediate (XXX.)

This was the first synthesis of a substance containing the intact carbon skeleton of brazilin.

Hæmatoxylin (XXIX), isolated from log-wood, is very similar to brazilin in its reactions. Perkin's researches on hæmatoxylin covered the whole field of oxidation products and other derivatives which had been obtained from brazilin and complete analogy was demonstrated. There is therefore no need to give the whole of the details. The analogue of brazilic acid was not obtained, but hæmatoxylinic acid, parallel to brazilinic acid, was isolated from the products of the permanganate oxidation, and the lactone of dihydrohæmatoxylinic acid was synthesised. Hæmatein and its derivatives proved to be quite analogous to the brazilein series, while tetramethylhæmatoxylone was strikingly similar to trimethylbrazilone.

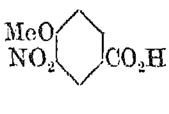
(6) *Harmine and Harmaline.*

Most of the important earlier work on the alkaloids harmine, $C_{13}H_{12}ON_2$, and harmaline, $C_{13}H_{14}ON_2$, was carried out by O. Fischer and his collaborators. They are mono-acid, optically

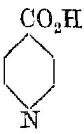
inactive bases and contain a methoxyl group; harmaline is dihydro-harmine and yields harmine on oxidation with dilute nitric acid. Oxidation of either base with chromic acid affords harminic acid, $C_8H_6N_2(CO_2H)_2$, which contains no methoxyl group and, when heated, loses carbon dioxide with formation of *apo*harminecarboxylic acid, $C_8H_7N_2{\cdot}CO_2H$, and then *apo*harmine, $C_8H_8N_2$. The oxidation could therefore involve the destruction of a benzene ring bearing the methoxyl, and this view was confirmed by the isolation of 3-nitroanisic acid (I) from among the products of the oxidation of harmaline with nitric acid. It was later (1914) found that *iso*-nicotinic acid (II) is formed from harminic acid by oxidation with dilute nitric acid in a sealed tube. O. Fischer also replaced the methoxyl group of harmine by a hydrogen atom, giving a base, $C_{12}H_{10}N_2$, called harman. These were the main features which had been established when Perkin and Robinson embarked upon the researches now to be described. The first advance which was made was the discovery that harmine contains a methyl group similar in reactivity to that occurring in quinaldine. The base condenses with benzaldehyde yielding benzylideneharmine, $C_{12}H_9ON_2{\cdot}CH{:}CHPh$, and this can be oxidised to norharminecarboxylic acid,

$$C_{12}H_9ON_2{\cdot}CO_2H,$$

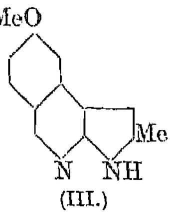
which in turn can be decarboxylated to give norharmine, $C_{12}H_{10}ON_2$, a base which resembles harmine in many respects. It thus became clear that harmine must be the methylmethoxy-derivative of a base, $C_{11}H_8N_2$, which might be called norharman, and it seemed likely that he ring system of this base is formed by the fusion of benzene, pyrrole, and pyridine nuclei, as in the structure (III) suggested for harmine in 1912 (*J.*, **101**, 1775).



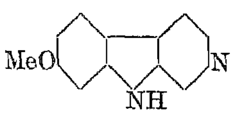
(I.)



(II.)



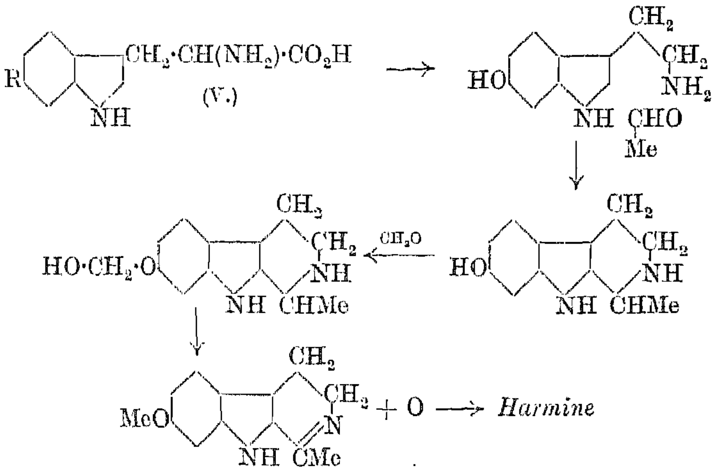
(III.)



(IV.)

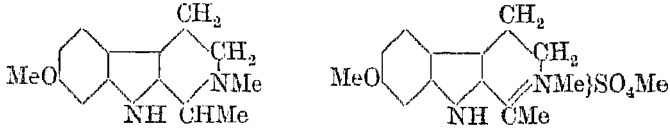
This idea stimulated synthetical investigations which resulted in the preparation of substances closely related to (III) (*J.*, 1913, **103**, 1973), but a further consideration of the implications arising from the isolation of nitroanisic acid (I) and *iso*nicotinic acid (II) during oxidative processes led in 1919 to the view that the expression (IV)

for norharmine was much more probable (*J.*, 1919, 115, 933). The belief that the benzene ring has a nitrogen atom attached in the position shown was experimentally confirmed by the observation that tetrahydroharmine couples with diazobenzenesulphonic acid to an azo-compound which exhibits a behaviour as an indicator similar to that of methyl-orange. In order to derive the harmine formula from that of norharmine a methyl group must be introduced next to the nitrogen of the pyridine nucleus and in this connection it was noted that the proposed new structures were closely related to that of the natural amino-acid tryptophan (V; R = H). The conviction grew that this was no mere coincidence and that the biogenesis of the alkaloids is probably from a hydroxytryptophan (V; R = OH), and the following scheme was advanced :



Harmaline

The position of the methyl group demanded by this hypothesis was also in agreement with the results obtained in studying the oxidation

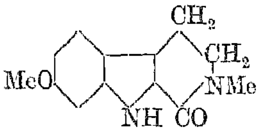


(VI.) (VII.)

of *N*-methyltetrahydroharmine (VI) and of harmaline methosulphate (VII) by means of potassium permanganate in acetone solution. A

neutral compound, $C_{13}H_{14}O_2N_2$, m. p. 228°, was obtained in both cases and this was best formulated as (VIII) on account of its failure to react with phosphorus pentachloride.

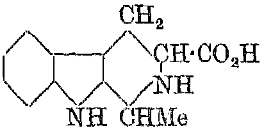
The most convincing proof of the general accuracy of the above suggestions was forthcoming as the result of a consideration of the probable nature of a base $C_{12}H_{10}N_2$, obtained by Hopkins and Cole (*J. Physiol.*, 1903, 29, 451) by the oxidation of tryptophan with ferric chloride. It was obvious that the carboxyl group of the amino-acid must have been eliminated and in that case two carbon atoms had been added to the molecule. These, it was thought, might have arisen from ethyl alcohol, because the solution had been extracted



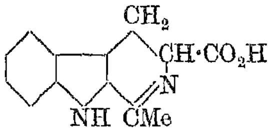
(VIII.)

(IX.)

with ether and then allowed to remain overnight. In other words it seemed possible that the base might have the constitution (IX), and this formula had already been regarded as the most probable representation of harman, prepared by O. Fischer; a direct comparison then established the identity of the base of Hopkins and Cole with harman (*J.*, 1919, **115**, 967).



(X.)

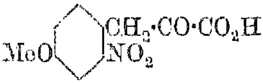


(XI.)

Somewhat later the conversion of tryptophan into harman (IX) was accomplished by a variety of methods (Kermack, Perkin, and Robinson, *J.*, 1921, **119**, 1602), including condensation with acetaldehyde to give (X), followed by oxidation, and, what amounts to the same thing, the oxidation of a mixture of tryptophan and alanine in acid solution. A reaction analogous to the Bischler–Napieralski synthesis of *iso*quinoline derivatives was also realised. Tryptophan was acetylated by means of acetic anhydride in the presence of zinc chloride with the formation of (XI), which was then oxidised. By substituting formaldehyde for the acetaldehyde in these syntheses, *nor*harman (XII) was obtained, and the same substance was derived from harmine by two routes. In the first place

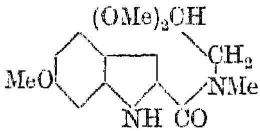
*nor*harmine was converted into *nor*harmol by demethylation and then reduced by heating with zinc dust in a stream of hydrogen. Secondly, harman was condensed with benzaldehyde, the product oxidised to *nor*harmancarboxylic acid and decarboxylated to *nor*-harman.

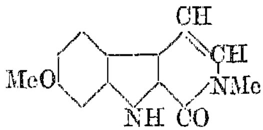

(XII.)


(XIII.)

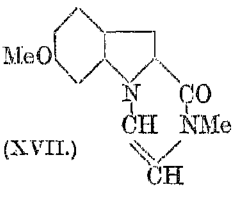

(XIV.)

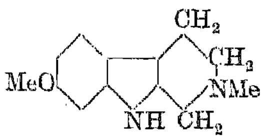
Further synthetical work included a proof of the position of the methoxyl group in the harmine molecule. *o*-Nitro-*p*-methoxy-phenylpyruvic acid (XIII), from the condensation of *o*-nitro-*p*-tolyl methyl ether with ethyl oxalate in the presence of alcoholic sodium ethoxide, was reduced with ferrous hydroxide to 6-methoxyindole-2-carboxylic acid (XIV), the chloride of which reacted with methyl-aminodimethylacetal to give the acetalylamide (XV). When this


(XV.)


(XVI.)

substance was treated with alcoholic hydrogen chloride, ring closure took place in both of the two possible directions to give a mixture of the products (XVI) and (XVII) which were separated and characterised by reference to related compounds of known constitution. Reduction of the former (XVI) with sodium and *n*-butyl alcohol then led to the base (XVIII) which was proved to be identical with the reduction product of *nor*harmine methosulphate (Kermack, Perkin, and Robinson, *J.*, 1922, **121**, 1872).


(XVII.)

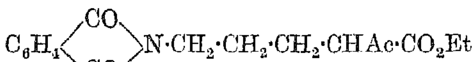

(XVIII.)

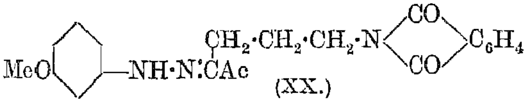
Finally, harmaline itself was synthesised (Manske, Perkin, and Robinson, *J.*, 1927, 1) starting from ethyl δ-phthalimido-α-acetyl-valerate (XIX) (Gabriel, *Ber.*, 1909, **42**, 1242), the process having

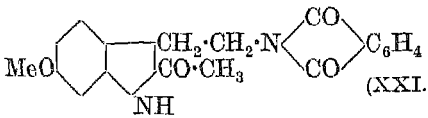
been first worked out in the simpler case of the hitherto unknown harmalan (XXIII), aniline being used instead of *m*-anisidine. The sodium salt, $CO_2Na{\cdot}C_6H_4{\cdot}CO{\cdot}NH{\cdot}[CH_2]_3{\cdot}CHAc{\cdot}CO_2Na$, derived from the substance (XIX) in cold aqueous-alcoholic sodium hydroxide, was coupled with *m*-anisyldiazonium hydroxide, and acidification then yielded the *m*-anisylhydrazone,

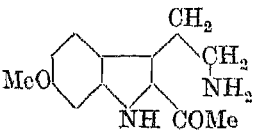
$$MeO{\cdot}C_6H_4{\cdot}NH{\cdot}N{:}CAc{\cdot}[CH_2]_3{\cdot}NH{\cdot}CO{\cdot}C_6H_4{\cdot}CO_2H,$$

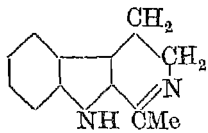
which gave the phthalimido-compound (XX) with acetic anhydride. Fischer's reaction was applied to this substance in boiling *n*-butyl-alcoholic hydrogen chloride with the formation of the indole (XXI). The direction of indole ring-closure was ambiguous, but justification for the formula (XXI) was provided by establishing the course of the Fischer reaction when applied to a closely related *m*-anisylhydrazone. Harmaline then resulted from the removal of the phthaloyl group, the substance (XXII) being an intermediate product in this operation.


(XIX.)


(XX.)


(XXI.)


(XXII.)

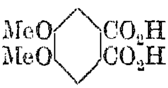

(XXIII.)

(7) *Cryptopine and Protopine.*

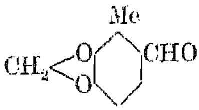
Cryptopine is a comparatively rare alkaloid, first isolated by J. Smiles from the mother-liquors obtained from opium extracts after the separation of morphine and thebaine. It was examined by Hesse (*Annalen, Suppl.*, 8, 300), who in 1872 assigned to it the correct composition, $C_{21}H_{23}O_5N$, and later found that it was optically inactive. Perkin in 1891 found that cryptopine furnished *m*-hemi-

pinic acid (I) on oxidation with potassium permanganate, but his more comprehensive investigations of the alkaloid may probably be dated from about 1910, and are described in two voluminous papers (*J.*, 1916, **109**, 815; 1919, **115**, 713). About this time Pictet and Kramers (*Ber.*, 1910, **43**, 132) secured indirect evidence that cryptopine contains a methylenedioxy-group and it was ascertained that the base is tertiary, contains a methyl group attached to nitrogen, and is difficult to reduce in acid solution. Crude dihydrocryptopine was obtained by Danckwortt (Habilitationsschrift, Breslau, 1912; *Arch. Pharm.*, 1912, **250**, 590) as the result of the action of sodium amalgam on a boiling solution of cryptopine in dilute sulphuric acid.

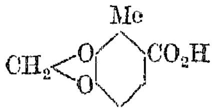
Perkin reduced cryptopine methosulphate in boiling acid solution by sodium amalgam with formation of tetrahydromethylcryptopine, $C_{22}H_{29}O_5N$, and this was dehydrated by means of acetyl chloride to anhydrotetrahydromethylcryptopine, $C_{22}H_{27}O_4N$. When this substance was oxidised by potassium permanganate in acetone solution it gave *m*-hemipinic acid (I), 5 : 6-methylenedioxy-*o*-tolualdehyde (II), the corresponding acid (III), and 4 : 5-dimethoxy-2-β-dimethylaminoethylbenzaldehyde (IV). The base (IV) was obtained among other products by the action of methyl iodide on 4 : 5-dimethoxy-2-



(I.)



(II.)



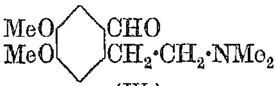
(III.)

β-methylaminoethylbenzaldehyde (V) (now regarded as a cyclic carbinol-amine), which Pyman (*J.*, 1909, **95**, 1272) obtained by the oxidation of laudanosine. The aldehyde (II) could be oxidised to the acid (III) and the methylenedioxy-groups in both substances were hydrolysed by Barger's method (*J.*, 1908, **93**, 572). The dihydroxytoluic acid was methylated and oxidised to hemipinic acid and, on the other hand, it was heated with water at 170—180° and then furnished 2 : 3-dihydroxytoluene. These facts were not easy to glean, but they established the constitution of these fundamental oxidation products.

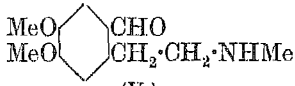
Now (IV) and (II) are obtained from anhydrotetrahydromethylcryptopine by addition of two atoms of oxygen and therefore this base must have the constitution (VI) and tetrahydromethylcryptopine must be (VII) or the alternative with the group $-CH_2{\cdot}CH(OH)-$

transposed. Actually (VII) is correct, a statement which is justified below.

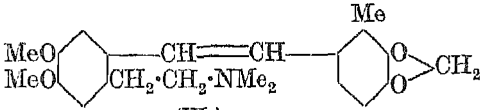
The Hofmann degradation of (VI) gave cryptopidene (VIII) and



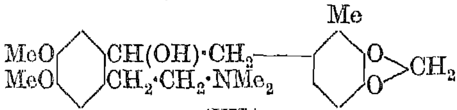
(IV.)



(V.)

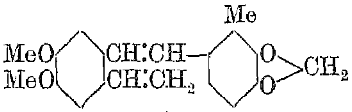


(VI.)



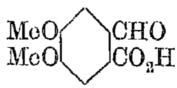
(VII.)

permanganate oxidation of this substance gave (I), (II), and (III), 4 : 5-dimethoxy-2-vinylbenzaldehyde (IX) and *m*-opianic acid (X).



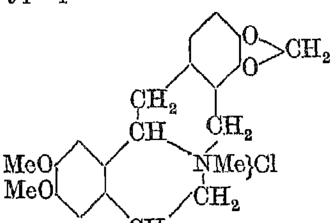
(VIII.)

(IX.)

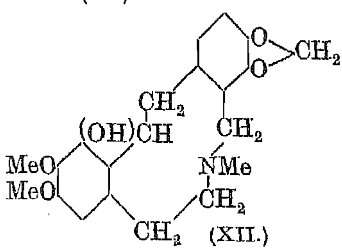


(X.)

The dihydrocryptopine of Danckwortt, when digested with acetyl chloride or phosphoryl chloride, was dehydrated with formation of two isomeric quaternary salts called the α- and β-*iso*dihydrocryptopine chlorides. These substances were so strikingly similar to the α- and β-methochlorides (XVII) of tetrahydroberberine (Pyman, *J.*, 1913, **103**, 825) and corresponded so closely to these substances in their chemical properties (a resemblance which received emphasis from a comparison of the behaviour of the corresponding hydroxides on dehydration) that there could be no doubt that the *iso*dihydrocryptopine chlorides have the constitution (XI) and are stereoiso-



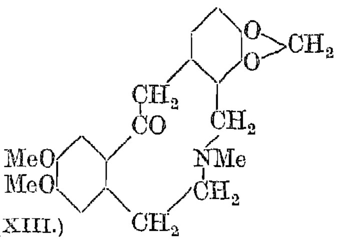
(XI.)



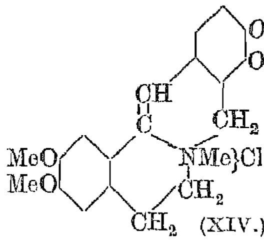
(XII.)

merides. This conclusion, amply confirmed by all later work, fixes the position of the hydroxyl group in tetrahydromethylcryptopine, and dihydrocryptopine was considered by Perkin to have the constitution (XII). The logical further step is that cryptopine itself must have the ten-ring formula (XIII) and this was adopted after some hesitation.

When cryptopine is digested with acetyl chloride or phosphoryl

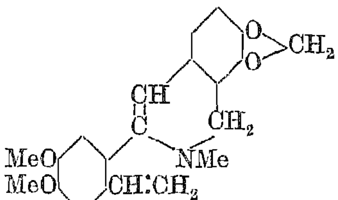


(XIII.)

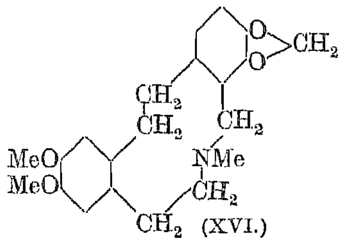


(XIV.)

chloride, it is converted into *iso*cryptopine chloride (XIV) and this interesting quaternary salt is converted by hot methyl-alcoholic potash into anhydrocryptopine (XV), the manifold transformations of which Perkin examined in great detail. Reduction of *iso*cryptopine chloride in acid solution led ultimately to dihydroanhydrodihydrocryptopine (A) (XVI), which was found to be remarkably stable towards permanganate.



(XV.)

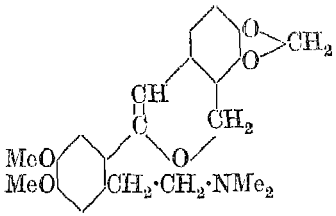


(XVI.)

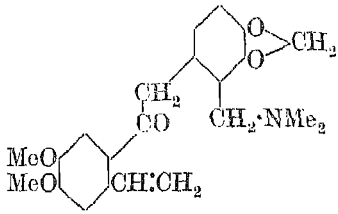
The decomposition of cryptopine metho-salts under various conditions led to the formation of the polymorphic methylcryptopines (α) and (β), and to methylcryptopine (γ) which, unlike (α) and (β), yielded a semicarbazone. On exhaustive methylation both the (β) and the (γ) form gave the same products, namely, cryptopidiol and its anhydro-derivative. The formulæ suggested for these substances are on page 216.

The epi*Berberine Derivatives.*—Reference has already been made to the connection between *iso*dihydrocryptopine chloride (XI) and

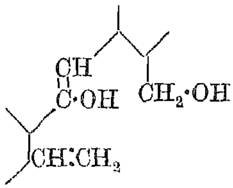
tetrahydroberberine methochloride (XVII). It will be observed that the methylenedioxy-groups and methoxy-groups are transposed



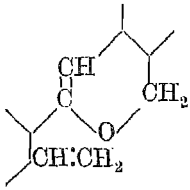
Methylcryptopine (β).



Methylcryptopine (γ).

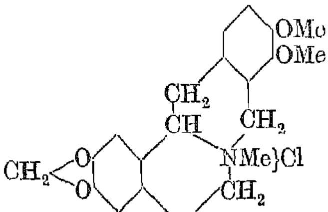


Cryptopidiol.

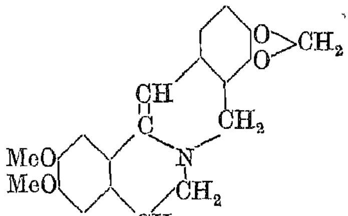


Anhydrocryptopidiol.

and in fact cryptopine corresponds to a substance which Perkin studied exhaustively (*J.*, 1918, **113**, 492) and which he named *epi*-

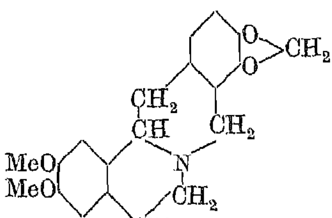


(XVII.)

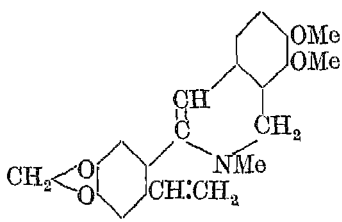


(XVIII.)

berberine. It was found that *iso*cryptopine chloride and *iso*dihydrocryptopine chloride decomposed smoothly on heating. The products



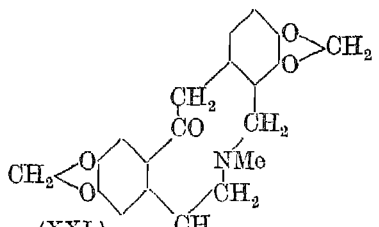
(XIX.)



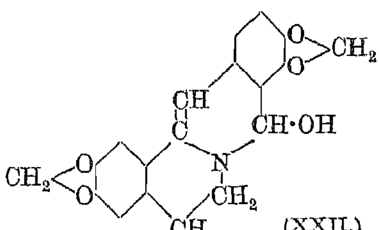
(XX.)

were methyl chloride and dihydroanhydro*epi*berberine (XVIII) and tetrahydroanhydro*epi*berberine (XIX) respectively. These bases

exhibited close resemblance to their berberine relations and a great tract of berberine chemistry was traversed in the *epi*berberine field. For example, *epi*berberinium salts and oxy*epi*berberine were prepared and examined. Similarly, derivatives of berberine allied to those of cryptopine were minutely examined (*J.*, 1918, **113**, 722). The starting point was, in this case, dihydroanhydroberberine, obtained by the action of potassium hydroxide on berberine itself. It is related to (XVIII) and on conversion into a methine it yielded anhydromethylberberine (XX), the opposite number of anhydrocrytopine in the berberine series.



(XXI.)



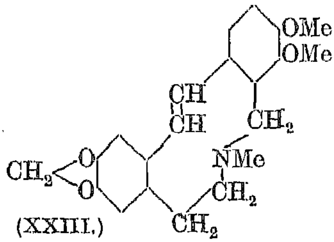
(XXII.)

Protopine.—This alkaloid is much more widely distributed in nature than cryptopine, but it is less accessible in quantity. Perkin succeeded in showing that every important derivative of cryptopine could be reproduced in the protopine series and that the difference resides merely in the fact that the methoxyl groups of cryptopine are replaced by a methylenedioxy-group in protopine. He showed by the clearest analogies that protopine has the constitution (XXI) and the related berberine-type base is coptisine (XXII), isolated by Kitasato from *Coptis japonica* (*Proc. Imp. Acad. Tokyo*, 1926, **2**, 124).

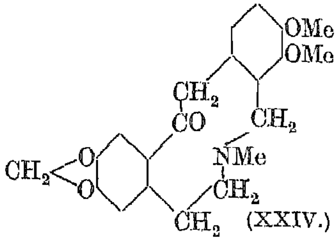
The alkaloid β-homochelidonine (XXIV) is the "cryptopine" of the berberine series. Thus in 1919 Gadamer (*Arch. Pharm.*, **257**, 298; also *ibid.*, 1920, **258**, 148) found that it was convertible into dihydroanhydroberberine methochloride exactly as cryptopine yields *iso*cryptopine chloride.

Synthesis of β-Homochelidonine, Cryptopine, and Protopine.—With the completion of the synthesis of oxyberberine and berberine, the earlier observations of Pyman (*J.*, 1913, **103**, 817), who had obtained the anhydro-base (XXIII) by the dehydration of tetrahydroberberine methohydroxide, pointed the way to the synthesis of β-homochelidonine. The base (XXIII) was oxidised in chloroform solution by means of perbenzoic acid. The product was the amine

oxide and this could be directly transformed into β-homochelidonine (XXIV) by treatment with a mixture of acetic and hydrochloric acids (Haworth and Perkin, *J.*, 1926, 445). Exactly similar methods



(XXIII.)

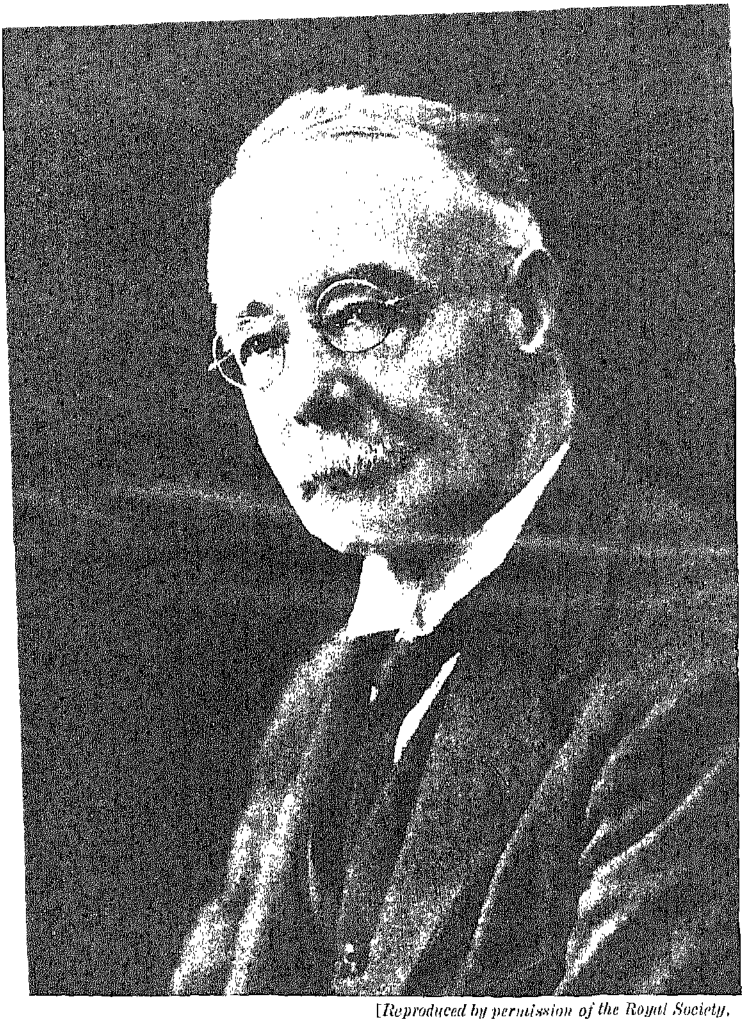


(XXIV.)

were applied for the synthesis of cryptopine and protopine (Haworth and Perkin, *J.*, 1926, 1769). The appropriate oxy*epi*berberine and oxycoptisine were prepared by the second of Perkin's oxyberberine syntheses, referred to in an earlier section; then the tetrahydro-bases, their methochlorides, anhydro-bases and amine oxides thereof were derived.

In conclusion mention may be made of two other fields to which Perkin devoted considerable attention. He was always attracted by stereochemical problems, the theory of which satisfied his demand for simplicity and definiteness. The reader can find elsewhere in this volume, in the section which deals with the work of Sir William Pope, an account of the classical researches of Perkin and Pope on the preparation and resolution of 1-methyl*cyclo*hexylidene-4-acetic acid.

During the last few years of his life Perkin was actively engaged in a study of the chemistry of strychnine and brucine; he made many important observations in this field, but the researches were far from complete at the time of his death. It is not possible in this short review to give a satisfactory account of his contributions to this very complex subject which had also attracted several other workers.



[*Reproduced by permission of the Royal Society.*

A. G. Perkin

ARTHUR GEORGE PERKIN

1861—1937

ARTHUR GEORGE PERKIN was born at Sudbury, Middlesex, on December 13th, 1861. He was the second son of the late Sir William Henry Perkin, F.R.S., who discovered mauveine and thereby founded the coal-tar colour industry in this country. His elder brother was the late William Henry Perkin, jun., F.R.S., Waynflete Professor of Chemistry in the University of Oxford, and the late Dr. Frederick Mollwo Perkin, C.B.E., who was well known as a consulting chemist, was his half-brother.

A. G. Perkin's mother died of consumption shortly after his birth, and he was such a delicate child that he was not expected to live. At about the time of Sir William's second marriage to Miss A. C. Mollwo, Perkin, at the age of six, was sent to a boarding-school at Margate and henceforth spent little time at home at Sudbury except during his holidays. At about the age of ten he entered the City of London School, where his brother William had already been a pupil for one year, this school having been selected for the boys, not merely because it was Sir William's old school, but also because it was the only one that he could find where science was taught at that period. The boys were fortunate to have as their science master there Henry Durham, who was an able and attractive teacher. It is said that one of the other masters, however, refused to have both Perkins in his class, so Arthur as junior had to give place to William and was transferred to another class.

During their holidays the boys carried out crystallisations and similar work given to them to do by Sir William in a small hut which he had had fitted up as a laboratory for their use at the bottom of the garden at Sudbury. William used a bench beneath a window at one end and Arthur used a bench beneath a window at the other end.

Consequently, it is no more surprising that chemical research should have become the prime object of the working lives of both boys, than that music should have become the principal recreation of their

leisure, for the Perkins were always an extremely musical family. Thus, during these holiday periods nine members of the family constituted a small orchestra, in which William played second violin and Arthur the flute. The family concerts usually took place on Saturdays at the house of the late Thomas D. Perkin, Sir William's brother and partner, and more formal concerts were also given occasionally.

In October, 1877, William entered the Royal College of Chemistry at South Kensington, and one year later Arthur followed him there to study under Frankland and Guthrie. Arthur worked at a bench next to that of Leo Stern, who later become a well-known player on the violoncello, so William, Arthur, and Stern soon formed a trio to play on Saturdays, and the two Perkins were also leaders in gathering together an orchestra largely consisting of students.

It was at the Royal College of Chemistry that Arthur carried out the investigation that led to his first paper, "The Action of Nitric Acid on Di-*p*-tolylguanidine", communicated to the Chemical Society in 1880.

Up to this stage the education of the two brothers had proceeded on similar lines, but their paths then diverged, for William at last received his father's permission to go to a German University, and he went to Würzburg in October, 1880, whereas Arthur went for one year to Anderson's College, Glasgow, under E. J. Mills.

In 1881 A. G. Perkin heard that the Worshipful Company of Clothworkers had instituted a scholarship for one year tenable in the Dyeing Department of the Yorkshire College, Leeds, and applied for it, the only other applicant being Charles Bedford of Leeds. They became fellow students and friends, but the scholarship was awarded to Perkin, who was thus the first of many Clothworkers' Scholars in the Department of which he eventually became the Head. He worked with the then Head of the Dyeing Department, J. J. Hummel, on some new compounds derived from the colouring matters of brazilwood and logwood. Throughout his life Perkin lost no opportunity of paying a generous tribute to the ability and personality of Prof. Hummel, to whom he owed his first introduction to, and enduring enthusiasm for, the study of the chemistry of natural colouring matters.

When his scholarship expired, Perkin left the Yorkshire College to take up an appointment as chemist at the alizarin factory of Hardman and Holden, Ltd., Manchester.

In 1887 he married Annie, a daughter of James E. Bedford of

Leeds and sister of Charles Bedford. As a bachelor he lived at Cheetham Hill, but after his marriage he lived at Eccles.

Perkin was promoted to the position of manager by Hardman and Holden, Ltd., in 1888 and continued in that capacity until 1892. During this period of ten years which he spent in industry, Perkin made time to carry out a number of scientific investigations and published papers on the action of nitric acid on anthracene, and, jointly with his brother William, on derivatives of anthraquinone, and on the Indian natural dyestuff, kamala.

In 1892 Perkin resigned his position with Hardman and Holden, Ltd., in order to join the staff of the Dyeing Department, Yorkshire College, as lecturer and research chemist. This position suited his tastes and temperament admirably, because, although he gave a course of lectures on the chemistry of natural colouring matters for one hour per week in the first and second terms of each session and also gave general supervision to the small number of senior students who did their practical work in the Clothworkers' Research Laboratory, he was able to devote all the rest of his time to his own investigations at a bench in this laboratory for the next twenty-two years. Nevertheless, there were not sufficient hours in a normal working day for him, so for a number of years at the outset he returned to the laboratory in the evenings, being then accompanied by his wife, who assisted him with his apparatus and with some of his experiments, and there they would usually remain until about 10 p.m. During this period of intensive research, with few exceptions, Perkin confined himself to the isolation of the colouring matters of a large number of natural products and the investigation of their constitutions, largely by degradative methods and by studying their dyeing properties. Synthetic work did not greatly appeal to him and he was content to leave to others the confirmation of his deductions. For example, the constitutions proposed by Perkin for apigenin, catechin, gossypetin, luteolin, morin, myricetin, and quercetagetin have since been confirmed synthetically by other workers.

The profound knowledge of natural colouring matters that Perkin gained by his brilliant researches established his international reputation in this field and brought many chemists from abroad, particularly from the East, to work at Leeds on natural products under his guidance.

In 1905 the India Office, on behalf of the Government of India, selected the Clothworkers' Research Laboratory as the most suit-

able place for the continuation of the research work on natural indigo that had been carried out by W. P. Bloxam and two colleagues on behalf of the Government of Bengal at the Dalsingh Serai Research Station from 1902 to 1904. Bloxam, assisted by four other chemists, worked on this subject at Leeds from 1905 to 1907 under the general supervision of Perkin. In his Report to the Government of India published in 1908, Bloxam made it very clear that Perkin by no means confined himself to the official limits of general supervision, but that he also devoted much of his time to experimental work on this subject. Thus, his examination of the constituents of natural indigo and their isolation led to a method for the estimation of the glucoside indican either in the crystalline condition or in aqueous infusions of the leaf, established that indirubin present in natural indigo arises from the condensation of indoxyl with isatin, the latter being produced by air oxidation of the former, and that indigo yellow is identical with kæmpferol.

Between 1904 and 1918 the late E. R. Watson, while he was Professor of Chemistry, first at Sidpur Engineering College and then at Dacca College, usually worked in the Clothworkers' Research Laboratory for a large part of his leaves in England in order to have the benefit of contact with Perkin, with whom he had so many research interests in common, and they became great friends.

During the War, Perkin carried out investigations for the Ministry of Munitions, and in 1916 he succeeded A. G. Green, F.R.S., as Professor of Colour Chemistry and Dyeing in the University of Leeds, at the same time also directing the work on intermediates and synthetic dyes carried out in his Department by the colony of research chemists of British Dyes, Ltd. It was this alteration in his position, with the consequent increase in his administrative and teaching duties, that gradually compelled Perkin to relinquish his work on natural colouring matters and to turn his attention again to the chemistry of anthraquinone derivatives, for which the starting materials were more readily accessible. Thus, a study of the migration of the acyl group in partly acylated phenolic compounds led to the preparation of interesting derivatives, many of which had not previously been obtained synthetically. The products of the reduction of hydroxyanthraquinone compounds also formed the subject of a notable series of papers published between 1922 and 1933. In the course of this work the constitutions of numerous hydroxyanthranols were established by conversion into corresponding benzanthrones and examination of the methylation products of the

latter, whilst the formation of hydroxy-anthracenes, -dianthrones, -dianthraquinones, -diathraquinonyls, and -helianthrones also was investigated and the constitutions of these compounds established.

During his professorship Perkin did much to enhance the reputation of his Department as a scientific training ground for recruits for the dyestuffs, dyeing, and allied industries. In the immediate post-War years there was a very considerable increase in the number of students who entered for courses in colour chemistry and dyeing, and there is no doubt that they were attracted at least as much by the opportunity of working under him as by the popular appeal of these subjects at that period. His students were uniformly successful in securing appointments, and most of them now occupy important positions in industry.

Perkin was elected a Fellow of the Chemical Society in 1884, a Fellow of the Institute of Chemistry in 1887, a Fellow of the Royal Society of Edinburgh in 1893, a Fellow of the Royal Society in 1903, and was awarded the Davy Medal of the Royal Society in 1924. Although he never took an active part in the affairs of scientific societies, he believed strongly in supporting them by membership: he was a vice-president of the Society of Dyers and Colourists, and a member of the Biochemical Society, the Pharmaceutical Society, the Society of Chemical Industry, and the Textile Institute. He was also a Liveryman of the Worshipful Company of Leathersellers, of which his father was Master at one time, and thereby a Freeman of the City of London.

On his retirement in 1926, Perkin was accorded the title of Emeritus Professor, and in 1927 the University of Leeds conferred upon him the degree of D.Sc., *honoris causa*. An admirable portrait of him was painted by Richard Jack as a result of the subscriptions of Perkin's many admirers and presented to the University of Leeds, where it graces the wall of the Great Hall.

Perkin regarded his retirement merely as freedom from the burden of administrative and teaching work and the opportunity to concentrate once more on his experiments. From the autumn of 1926 he continued to prosecute his researches without any interruption in the writer's laboratory in the Colour Chemistry and Dyeing Department of the University of Leeds until February 1937, when his health began to fail. He was then endeavouring to determine the constitution of a green vat dye which he had obtained some years previously by heating the hydroxylated anthranol, derived from alizarin, with tetrachlorothiophen and an alkylating

agent (B.P. 353,422). In spite of the preparation of a very large number of individual specimens of this dye, however, Perkin was unable to interpret the analytical results obtained with them to his satisfaction, and this apparently insurmountable difficulty worried him greatly, as it was contrary to his whole nature to allow himself to be beaten by a mere compound.

Perkin's health continued to decline slowly for about three months, during which he welcomed visits from his colleagues and enjoyed entertaining them with his vivid recollections of chemists and their work, but he collapsed suddenly on May 26th and died at his residence, Grosvenor Lodge, Grosvenor Road, Leeds, on May 30th, 1937.

Many representatives of the leading scientific societies, of the University of Leeds, of industry, and of his students paid respect to Perkin at the funeral service in St. Chad's Church, after which the interment took place at Adel Church, Leeds.

Perkin was an indefatigable worker and delighted in carrying out experiments with his own hands, it being only within recent years that he became resigned even to entrusting the necessary analyses of his new compounds to others; in earlier years he would not allow students near his melting-point apparatus or his analytical apparatus, so much did he dread interference with their adjustment. His technique was well-nigh flawless and his skill in isolating the required substance from a complex mixture almost uncanny. He appeared to be immune to any vapours; the atmosphere of his laboratory, often charged with the vapours of acetic anhydride, nitrobenzene, and pyridine, to an extent sufficient to induce nausea in the other occupants, left him unaffected, indeed it is doubtful whether his concentration on his work permitted him to notice this accumulation of odours. This deep absorption in his experiments and close attention to every detail, together with his infinite patience with difficult reactions or with tedious processes of purification of initially resinous materials, from which he would eventually isolate "beautiful crystals", gained for him the admiration of his colleagues and students. He made a deep impression on all who were privileged to work with him; he was eminently easy to approach, ever ready to discuss difficulties, and to offer from his great experience suggestions for new lines of attack, once he was satisfied that the lack of success was not attributable to "the personal equation"! He was a great chemist in his generation, who always sought to encourage, to stimulate to fresh effort, and to set by his example a standard of application that all who came in contact with him were inspired to emulate. In addition, although a man of deep convictions, he was

a very gentle man with a most charming and lovable personality. His attitude towards young men was always so fatherly that for over forty years all students of the Colour Chemistry and Dyeing Department showed their affection for him by referring to him amongst themselves solely as " Pa Perkin ".

Perkin's work is recorded in some 270 memoirs, of which twelve were published in the *Journal of the Society of Chemical Industry*, four in the *Journal of the Society of Dyers and Colourists*, and the rest in the *Proceedings* or *Transactions of the Chemical Society*; his work is permanently illustrated by a collection of research specimens in the Museum of the Colour Chemistry and Dyeing Department of the University of Leeds, adjacent to a collection of his father's research specimens. In addition, he was concerned in seven patents arising from his work since 1916. He was also the author of many articles on natural colouring matters in Thorpe's " Dictionary of Applied Chemistry ", and, in collaboration with Dr. A. E. Everest, he published the classical monograph " The Natural Organic Colouring Matters " in 1918.

Perkin was completely happy in his home during his fifty years of married life and he owed a great deal to his wife. Some forty years ago they built a house at Bradda in the Isle of Man and ever since then they spent almost all the vacations there. Perkin was very fond of the Isle of Man and was a governor of King William's College.

Perkin was deeply attached to animals and especially to his dogs and ponies, and his tortoise. He first kept King Charles spaniels, but for the last twenty years or so he kept only a succession of Japanese spaniels, each of which he named after Japanese Professors who had worked with him in the past and who greatly appreciated this token of remembrance. He kept his ponies in the Isle of Man, and the surviving one is to remain there. He was very proud of the good health and steady growth of the tortoise, which he had had for the last twenty-five years and which usually accompanied him to the Isle of Man in the vacations.

Although Perkin played golf and worked out exactly how it should be played, he had not the temperament to become a first class player. He remained a great lover of music throughout his whole life, and it was in music that he found his real recreation, devoting all his leisure to it. He was a very accomplished player on both the flute and the bassoon. Seldom a day passed, until a few weeks before his last illness, when he did not play one or other of these instruments for an hour or two. He played first bassoon in many amateur orchestras in Yorkshire until his retirement; subsequently he

assisted the Leeds University Students' Orchestra, and his flute solos were a feature of the annual gatherings of past and present students of the Colour Chemistry and Dyeing Department until as recently as 1935.

Scientific Work of A. G. Perkin.

Inclusive of Notes in the *Proceedings* of the Society, Perkin published about 270 original papers and more than sixty of his more substantial contributions are in his own name without collaborators. He worked best with his own hands, and his sincere and simple nature is reflected in his writings. He possessed in full measure the family aptitude for experimental research and the single-hearted devotion to it which characterised his elder brother.* Nevertheless Arthur's method and attitude were individual and by no means the same as William's. He was a little the slower of the two and he did not aim quite so high, but he became the acknowledged master of his chosen field, which may roughly be defined as that of the natural colouring matters which have adjective dyeing properties. His chief contribution was doubtless the elucidation of the chemistry of the constituents of certain dye-woods and the development of the group of the flavones and flavonols. All his work was meticulous and accurate, most of his conclusions have been justified by later studies and his records have not been challenged.

Early Investigations.—Whilst at the Royal College of Chemistry under Frankland and Guthrie, Perkin, at the age of nineteen, published his first paper "The Action of Nitric Acid on Di-*p*-tolylguanidine" (*J.*, 1880, 37, 696). He prepared the dinitro-derivative, and in the presence of alcohol found that the product was dinitro-*p*-tolylurea. The corresponding diamines were obtained on reduction. It is interesting to note that the two nitro-compounds were formulated as condensed ammonia types as follows:

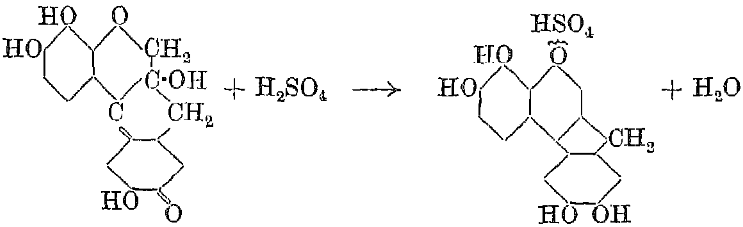
$$\left.\begin{array}{l} C_7H_6(NO_2) \\ C_7H_6(NO_2) \\ C^{iv} \\ H_3 \end{array}\right\} N_3 \qquad\qquad \left.\begin{array}{l} H \\ C_7H_6(NO_2) \\ CO \\ C_7H_6(NO_2) \\ H \end{array}\right\} N_2$$

* The writer first heard of A. G. P. from W. H. P. and the description given was "a dab hand"; this was but one of many indications of the mutual respect that subsisted between the brothers. On many occasions William assisted Arthur in such matters as the preparation of papers for publication and it is within the writer's knowledge that Arthur's advice was frequently sought by William and found to be most valuable.

At the Yorkshire College he worked with J. J. Hummel, and a joint paper published as a contribution from the Dye-House is of great interest. Perkin and Hummel (*J.*, 1882, 41, 367) improved the preparation of hæmatein and brazilein and showed that, when these substances were heated with sulphuric acid, a reaction occurred which was represented in the following manner :

$$\underset{\textit{hæmatein}}{C_{16}H_{12}O_6} + H_2SO_4 = \underset{\text{iso}\textit{hæmatein sulphate}}{\left.\begin{matrix}H\\C_{16}H_{11}O_5\end{matrix}\right\}SO_4} + OH_2$$

*iso*Hæmatein sulphate (and the corresponding *iso*brazilein sulphate) was isolated as an orange crystalline powder by the addition of acetic acid to the solution. The sulphuric acid was found to be loosely combined, and the substances were thought to be acid sulphuric ethers of a specially labile kind. We now know that the compounds in question are oxonium salts formed in accordance with the expressions :



Although Perkin and Hummel did not recognise the saline nature of the substances, they correctly stated that they were analogous to the acid compounds of the phthaleins which had been studied by Baeyer.

In 1883 Perkin followed up his father's work on xanthone, of which he prepared dinitro-, diamino-, and dibromo-derivatives (*J.*, 1883, 43, 187). A by-product from the distillation of a mixture of salicylic acid and acetic anhydride was thought to be $C_{14}H_8O_3$; it yielded xanthonecarboxylic acid when treated with alcoholic potash.

The first joint papers of the Perkin brothers deal with the products of the dry distillation of " silver salt " or sodium anthraquinone-2-sulphonate (*J.*, 1885, 47, 679; 1888, 53, 831). They obtained in this way a red compound, which was examined in some detail, but the fact that it contained sulphur was overlooked ! The sequel to

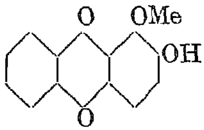
this curious and unique incident occurred thirty-four years later when A. G. Perkin disclosed that the substance is di-β-anthraquinonyl sulphide.

The action of nitric acid on anthracene under various conditions was the subject of some interesting work. In nitrobenzene solution the product was found to be nitrosonitroanthrone (*J.*, 1891, **59**, 631), but in the presence of alcohol, nitroethoxydihydroanthracene was produced. The behaviour of these substances towards reagents was investigated, and in collaboration with J. E. Mackenzie (*J.*, 1892, **61**, 470) the formation of nitroalkyloxydihydroanthracenes was extended by the use of alcohols other than ethyl alcohol. With *iso*butyl alcohol the product was nitroanthrone, and with *tert.*-butyl alcohol, nitrosoanthrone was produced; otherwise the formation of nitroalkyloxydihydroanthracenes was generalised. Other work of this period (partly at the Heriot Watt College) was concerned with derivatives of oxanilide, but the year 1893 may be taken as the starting point of Perkin's main work on natural colouring principles.

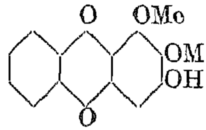
One of the first, if not the very first, problem selected was the nature of the constituents of the Indian dye, kamala, and preliminary work on this subject was published jointly with W. H. Perkin, jun. (*Ber.*, 1886, **19**, 3109). The more complete later papers (*J.*, 1893, **63**, 975; 1895, **67**, 230) are by A. G. Perkin alone. Anderson had already isolated a crystalline colouring matter which he termed rottlerin, and Perkin improved the method of extraction and obtained also the yellow homorottlerin, *iso*rottlerin, and a resin. To rottlerin, which gave crystalline acetyl and benzoyl derivatives and a number of crystalline metallic salts, Perkin assigned the formula $C_{33}H_{30}O_9$. On fusion with alkali, phloroglucinol and acetic and benzoic acids were obtained; oxidation with hydrogen peroxide gave benzaldehyde and benzoic acid, and treatment with nitric acid gave a variety of products, including *p*-nitrobenzaldehyde and *o*- and *p*-nitrocinnamic acids. Perkin concluded that rottlerin contains a phloroglucinol nucleus and a cinnamic acid residue. The difficult problem has not yet been completely solved, although the formula proposed by Robertson is doubtless a close approach to the truth. Perkin found that when the salmon-red rottlerin is heated with 2% sodium carbonate solution, garnet-red prisms of rottlerone separate. As the dyeing of silk to a bright orange shade is carried out with kamala in an alkaline bath, Perkin and Hummel (1895) point out that the colour fixed on the fibre is probably rottlerone.

Natural Colouring Matters of the Anthraquinone Group.

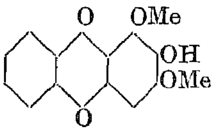
Largely in collaboration with Hummel, the constituents of dyeing materials similar to madder were examined. For example, Chay root or Indian madder was found to contain ruberythric acid, alizarin, rubichloric acid, and sucrose, but no purpurin or its carboxylic acid, or purpuroxanthincarboxylic acid. The non-tinctorial constituents were distinct from those occurring in madder; they included alizarin methyl ether (I), anthragallol dimethyl ether-A (II), anthragallol dimethyl ether-B (III), hystazarin methyl ether (IV), and 2-hydroxyanthraquinone (Perkin and Hummel, *J.*, 1893, **63**, 1160; 1895, **67**, 817; A. G. Perkin, *J.*, 1907, **91**, 2066).



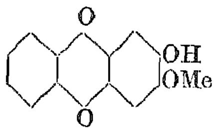
(I.)



(II.)



(III.)



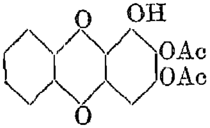
(IV.)

Much later a study of the partial acetylation of hydroxyanthraquinones and the action of diazomethane on the acetyl derivatives, with or without migration of an acetyl group, led to the syntheses of these compounds.

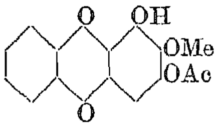
Oesch and Perkin (*Proc.*, 1914, 30) treated monoacetylalizarin with diazomethane in nitrobenzene solution and after hydrolysis isolated the isomeric alizarin monomethyl ethers. They interpreted this result as due to the fact that the monoacetyl derivative was a mixture, but in view of the later work it is probable that this was not so and that migration occurred. The *O*-methylalizarin from Chay root is the 1-methyl ether, because the 2-methyl ether is formed in the partial methylation of alizarin (and by analogy the hydroxyl ortho to carbonyl is protected) and also because it is very readily hydrolysed to alizarin, for example, by means of boiling aqueous baryta. In confirmation the alizarin 1-methyl ether is readily methylated with formation of alizarin dimethyl ether.

The syntheses of the isomeric anthragallol dimethyl ethers were

effected in an interesting manner (Perkin and Kubota, *J.*, 1925, **127**, 1889; Perkin and Storey, *J.*, 1928, 229; 1929, 1399). Anthragallol 2 : 3-diacetate (V) was found to be methylated in position 2 by means of diazomethane; at the same time the acetyl group migrates to position 1. Hydrolysis and partial acetylation affords (VI), which is methylated by diazomethane with the formation of the acetyl derivative of anthragallol 1 : 2-dimethyl ether. Anthragallol 2 : 3-dimethyl ether can be obtained by direct methylation of anthragallol.



(V.)



(VI.)

Perkin and Hummel (*J.*, 1893, **63**, 115) detected the presence of purpuroxanthin in *Rubia cordifolia* (Linn.) and found that the dyeing properties of *Rubia Sikkimensis* (Kurz) are due to its content of purpurin (*ibid.*, p. 1157). They also examined various species of *Morinda* and showed that the methylanthracene previously derived by Thorpe and Smith by zinc dust distillation of morindon is 2-methylanthracene (*J.*, 1894, **65**, 851). *Polygonum cuspidatum* was found to be a source of a glucoside of emodin (Perkin, *J.*, 1895, **67**, 1084).

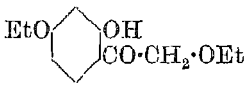
The root bark of *Ventilago madraspatana* (Gaertn.) was found to contain 8—10% of a resinous colouring matter, ventilagin, which is a derivative of 1-methylanthracene. Its composition was stated to be $C_{15}H_{14}O_6$ and the suggestion was made that it may be allied to alkannin (Perkin and Hummel, *J.*, 1894, **65**, 923). This root bark also afforded an emodin monomethyl ether and two isomeric anthranols which yield the emodin derivative on oxidation.

Flavones and Flavonols.

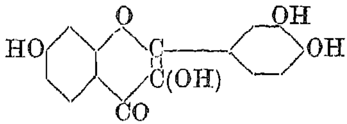
In 1864 Piccard isolated chrysin, $C_{15}H_{10}O_4$, from poplar buds and showed that on hydrolysis with alcoholic potash it yielded phloroglucinol, acetophenone, acetic and benzoic acids. These facts were confirmed in 1893 by v. Kostanecki, but the pioneering researches of Herzig on the constitution of fisetin and of quercetin gave the first real insight into the nature of this group of anthoxanthins. Herzig commenced his work in 1884 and determined the structure of fisetin in 1891. In the same year he established the composition of

quercetin, which had been in some doubt, and suggested the formula at present accepted, partly by analogy with fisetin.

Herzig ethylated fisetin and showed that on hydrolysis with alcoholic potash the tetraethyl ether afforded fisetol diethyl ether (VII) and 3 : 4-diethoxybenzoic acid. Hence fisetin was regarded as a tetrahydroxyphenylbenzo-γ-pyrone (VIII), and quercetin, so similar to fisetin in all its properties, was considered to be the corresponding phloroglucinol derivative.



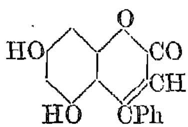
(VII.)



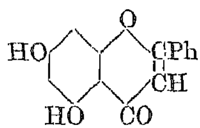
(VIII.)

v. Kostanecki's procedure with chrysin, two years later, was so logical and so well followed up in other cases that it has often been expounded as if it constituted the beginning of the subject, and there has been a tendency to overlook the work of Herzig.

He pointed out that the products of hydrolysis of chrysin could be explained on the basis of two formulæ (IX and X). He therefore excluded (IX) by synthesis of this coumarin derivative, following the method of v. Pechmann. The comparatively recent work of Wilson Baker has shown that this step was necessary because coumarins constituted like (IX) do afford phloroglucinol on hydrolysis.



(IX.)



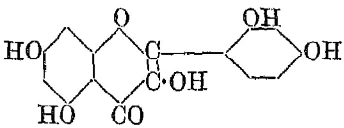
(X.)

The synthesis of (X), which proved to be identical with chrysin, followed in 1898.

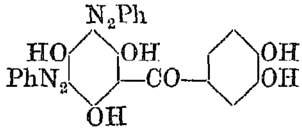
Accordingly when Perkin began his investigations (or rather when he published them) the nature of fisetin, quercetin, and chrysin was understood; his special contribution was the great extension of the group which he made and the development of new methods of investigation. One of the earliest of Perkin's researches in this field concerned the constitution of morin, which had been isolated by Chevreul from the wood of *Chlorophora tinctoria* (Gaudich); this dye-wood is termed "old fustic", and until recently was largely used.

Perkin and Bablich (*J.*, 1896, **69**, 792) improved the method of isolation of morin, determined its composition, and prepared numerous derivatives. On hydrolysis of the tetramethyl ether, 2 : 4-dimethoxybenzoic acid and phloroglucinol monomethyl ether were produced, and hence the formula (XI) was assigned to the substance. This was proved to be correct by the synthesis of the substance by v. Kostanecki, Lampe, and Tambor in 1906 as well as by a study of morin pentamethyl ether by Herzig in 1909. The hydrolysis of this derivative gave the methoxyfisetol dimethyl ether which had previously been obtained from quercetin pentamethyl ether.

It may be mentioned at this point that Perkin and Pate (*J.*, 1895, **67**, 649) examined the compounds formed by many members of the flavone group with mineral acids. The analysis of these substances often afforded valuable confirmation of the composition of the colouring matters themselves. In the case of morin the hydrochloride, hydrobromide, and hydriodide corresponded to the expression $C_{15}H_{10}O_7,HX$, but the sulphate was abnormal. Another type of derivative useful both for purposes of isolation and for analysis is represented by the monopotassium salt of morin, which separates when the substance is treated with potassium acetate in alcoholic solution (*J.*, 1899, **75**, 437).



(XI.)

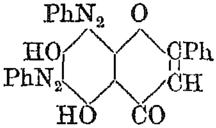


(XII.)

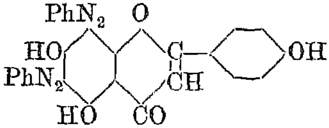
In addition to morin, old fustic contains a pentahydroxybenzophenone termed maclurin, and Perkin's brother-in-law, Mr. C. S. Bedford, found in 1887 (E.P. 12,667) that a valuable dye could be prepared by coupling this substance with diazonium salts. By the action of diazotised aniline on the water-soluble constituents of old fustic a dye called "patent fustin" was produced; it gave orange-brown shades on chrome-mordanted wool. The dye* is essentially bisbenzeneazomaclurin (XII) and the pure substance was prepared and examined by Bedford and Perkin (*J.*, 1895, **67**, 933; 1897, **71**, 186); it yields a triacetate when treated with acetic anhydride, which is in harmony with the proposed constitution and the monoacetylation of bisbenzeneazophloroglucinol. The azo-derivatives of other natural colouring matters were prepared by

Perkin (*J.*, 1898, **73**, 665), and he found them useful for the diagnosis of the phloroglucinol nucleus. For example bisbenzeneazochrysin (*J.*, 1896, **69**, 1439) (XIII) cannot be acetylated and bisbenzeneazoapigenin (*J.*, 1897, **71**, 805) (XIV) forms a monoacetyl derivative.

Another use of azo-compounds made by Perkin was in the recognition of the oily phloroglucinol monomethyl ether in the form of its bisbenzeneazo-derivative. Perkin and Allison (*J.*, 1902, **81**, 471) showed in this way that the quercetin tetramethyl ether obtained by direct methylation of quercetin is hydrolysed by alcoholic potash with formation of phloroglucinol monomethyl ether (and veratric acid).



(XIII.)



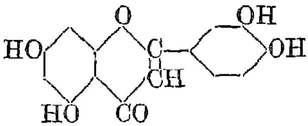
(XIV.)

It is difficult to give the exact chronological sequence of Perkin's researches of this period because it is very probable that several investigations were proceeding simultaneously. It would appear, however, that the elucidation of the constitution of luteolin preceded that of apigenin.

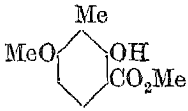
Weld is the oldest European dye (prepared from *Reseda luteola*); it was used by the Gauls in the time of Julius Cæsar, and its last surviving use was to produce lemon-yellow shades (aluminium mordant) on the silk facings of certain military uniforms.

Luteolin had been previously studied by Chevreul, Moldenhauer, Schützenberger, and Hlasiwetz, and the last-named assigned to it the composition $C_{15}H_{10}O_6$. Nothing was known, however, in regard to its constitution. Perkin (*J.*, 1896, **69**, 206, 799; 1900, **77**, 1315) isolated the principle by a novel method and effected a final purification from a trace of apigenin by the preparation of the hydrochloride. From a study of the numerous derivatives (sulphate, hydrochloride, hydrobromide, hydriodide, monopotassium salt, dibromo-derivative, tetra-acetate, trimethyl ether and its monoacetate, ethyl ethers and bromo- and nitro-derivatives of the ethers, etc.) and the alkali-degradation to phloroglucinol and protocatechuic acid, Perkin (*loc. cit.*) assigned to luteolin the constitution (XV). The correctness of this view was later confirmed by synthesis (Kostanecki, Rozycki, and Tambor, *Ber.*, 1900, **33**, 3410). Perkin and Horsfall (*J.*, 1900, **77**, 1322) showed that the decomposition of

luteolin with 50% aqueous potassium hydroxide afforded 3 : 4-dihydroxyacetophenone in addition to phloroglucinol.



(XV.)

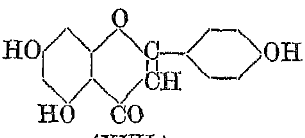


(XVI.)

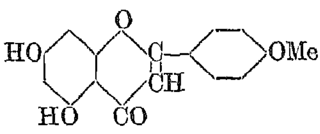
Perkin and Horsfall also observed that the methylation of luteolin with methyl iodide and alcoholic potash gives, in addition to the trimethyl ether, a methyl-luteolin trimethyl ether. The methyl group entered the phloroglucinol nucleus, because alkaline degradation led to the formation of methylphloroglucinol methyl ether, identified as its bisbenzeneazo-derivative. Methyl-luteolin was prepared by demethylation of the methyl ether. Similar nuclear methylation was noted by Perkin in the cases of several other flavones and flavonols, and he made a special study of it in the resorcinol series (*J.*, 1895, **67**, 990). Thus the methylation of methyl β-resorcylate by the usual process was proved to give rise to (XVI) in addition to the normal products.

The researches of von Gerichten on apiin, the glucoside occurring in the leaves, stem, and seed of parsley, rank in importance with those of Piccard on chrysin, but it was Perkin who showed that apigenin, the aglucone, is a member of the flavone group. As the result of the preparation of derivatives and their alkaline degradation he allocated the formula (XVII) to the substance, and this was later confirmed by syntheses due to other investigators.

The natural flavone, acacetin (*ex Robinia pseud-acacia* Linn.), was examined by Perkin (*J.*, 1900, **71**, 430) and shown to be apigenin methyl ether (XVIII). This substance was later synthesised.



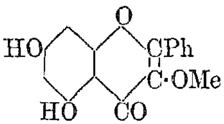
(XVII.)



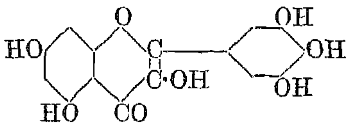
(XVIII.)

The flowers of the same plant were found to contain a remarkable glucoside termed robinin (Perkin, *J.*, 1902, **81**, 473). On hydrolysis it furnishes two molecules of rhamnose, one of glucose, and kæmpferol. The last is the flavonol corresponding to apigenin. Both this substance and its monomethyl ether, kæmpferide, were

studied by Perkin, who encountered them as constituents of various plants, but our knowledge of these flavonols is primarily due to v. Kostanecki. Incidentally it may be mentioned that the flavonol corresponding to chrysin is galangin (*ex* galanga root) and a congener is a galangin methyl ether (Testoni, *Gazzetta*, 1900, **30**, ii, 327). Perkin and Allison (*J.*, 1902, **81**, 470) found that, when air was aspirated through an alkaline solution of the methyl ether, phloroglucinol and benzoic acid were obtained and hence the methyl ether is the 3-derivative (XIX). This was later confirmed by synthesis. Perkin made frequent use of this method of oxidation in order to distinguish between flavones, which are unattacked, and flavonols, which are degraded, and the case of galangin methly ether is evidence that the distinction applies even to the 3-substituted flavonols.

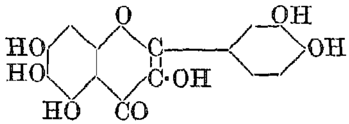


(XIX.)

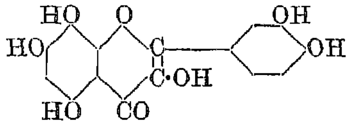


(XX.)

Employing similar methods Perkin in 1902 (*J.*, **81**, 203; also 1911, **99**, 1721) showed that myricetin, isolated from *Myrica nagi* in collaboration with Hummel (*J.*, 1896, **69**, 1287), is a flavonol of the constitution (XX). The constitutions of the isomerides of myricetin, namely, quercetagetin (XXI) from the African marigold and gossypetin (XXII) from cotton flowers, were partly established by Perkin (*J.*, 1899, **75**, 826; 1913, **103**, 209, 650), who regarded them as hydroxyquercetins and proposed the constitutions shown below.



(XXI.)

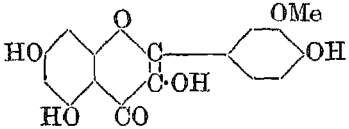


(XXII.)

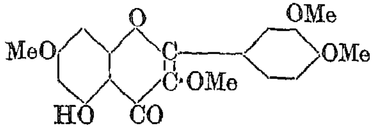
The suggestion could only be tentative because a hydroxyquercetin which should be either (XXI) or (XXII) had been described and this substance differed from the two flavonols in question. The erroneous character of this work and the correctness of Perkin's views were later demonstrated by the syntheses of gossypetin and quercetagetin.

Finally, mention may be made of *iso*rhamnetin (XXIII), first isolated by Perkin and Hummel from yellow wallflowers (*J.*, 1896,

69, 1566) and later by Perkin and Pilgrim from *Delphinium zalil* (*J.*, 1898, **73**, 268). Its constitution was determined by correlation with quercetin and by degradation to vanillic acid. The substance has been synthesised by an unambiguous method. Other quercetin methyl ethers were isolated from Persian berries (Perkin and Geldard, *J.*, 1895, **67**, 500).



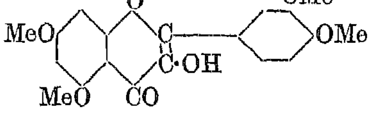
(XXIII.)



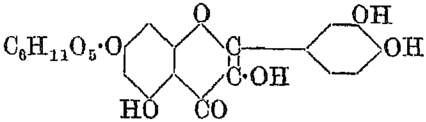
(XXIV.)

Quercetin Glucosides.—In addition to the aglucones Perkin studied the glucosides themselves in many cases and he extended the method of Herzig and Schönbach (*Monatsh.*, 1912, **33**, 678), who had shown that quercitrin is the 3-rhamnoside of quercetin. Direct methylation of quercetin affords the 3 : 7 : 3′ : 4′-tetramethyl ether (XXIV), whereas an intermediate in Kostanecki's synthesis is the 5 : 7 : 3′ : 4′-tetramethyl ether (XXV). Herzig showed that fully methylated quercitrin gives (XXV) on hydrolysis.

Perkin and Attree (*J.*, 1927, 234) found in this way that rutin, xanthorhamnin, and *iso*quercitrin are also 3-saccharides of quercetin but quercimeritrin is the 7-glucoside (XXVI). By full methylation and hydrolysis it furnished the hitherto unknown 3 : 5 : 3′ : 4′-tetramethyl ether of quercetin. The transposition of sugar groups in this series has been effected by Zemplén. Acetylated quercitrin (rhamnoside) is subjected to cautious acid hydrolysis with formation of tetra-acetylquercetin; the free hydroxyl group in the 3-position is then glucosidated, and the product hydrolysed by alkali. The resulting quercetin 3-glucoside accompanies quercimeritrin in cotton flowers (cf. Perkin, *J.*, 1909, **95**, 2181).



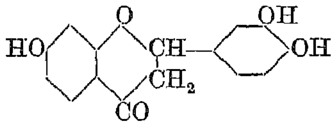
(XXV.)



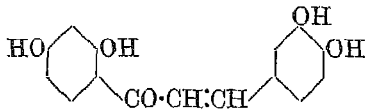
(XXVI.)

Natural Products related to the Flavones.

Perkin and Hummel (*J.*, 1904, **85**, 1459) found in the flowers of *Butea frondosa* a colourless substance, termed butin, which was recognised as a flavanone of the formula (XXVII). On hydrolysis and in the dye-bath it is converted into the isomeric butein (XXVIII). Condensation of pæanol with veratraldehyde gave butein trimethyl ether and this was changed to butin trimethyl ether by the action of dilute alcoholic sulphuric acid.



(XXVII.)



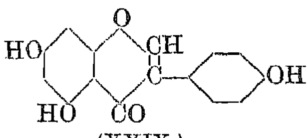
(XXVIII.)

The occurrence of this simple flavanone in Nature is of considerable interest.

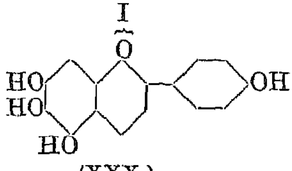
When a solution of butein in acetic acid is warmed with a few drops of sulphuric acid, a crystalline substance possessing beetle-green iridescence separates. This dissolves in alkalis to deep blue solutions and dyes mordanted fabrics in similar shades to those produced by anthragallol. The tentative explanation of Perkin is rather improbably correct and the matter is worthy of further investigation.

Genistein isolated along with luteolin from dyer's broom (*Genista tinctoria*) (Perkin and Newbury, *J.*, 1899, **75**, 830; Perkin and Horsfall, *J.*, 1900, **77**, 1310) was for some time considered to be a coumaranone derivative. Long before the syntheses demonstrated the fact, the late Professor told the writer that he knew that prunetin (Finnemore) was genistein methyl ether, but this idea was never published.

Perkin and Horsfall degraded genistein dimethyl ether by treatment with alkalis to phloroglucinol monomethyl ether and *p*-methoxyphenylacetic acid, and these results are in harmony with the *iso*flavone constitution (XXIX).

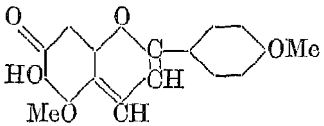


(XXIX.)

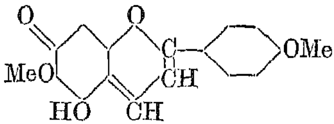


(XXX.)

A unique colouring matter from every point of view was isolated by Perkin from Chica Red (Perkin, *Proc.*, 1914, 30, 212). This is a cosmetic pigment used by the natives of the Upper Orinoco and it is derived from a species of *Bignonia*. The main constituent is a red crystalline substance termed carajurin; it is a dimethoxy-compound of the formula $C_{17}H_{14}O_5$ and is the colour base of flavylium salts. On demethylation by means of hydriodic acid, scutellareinidin iodide (XXX) is produced (Chapman, Perkin, and Robinson, *J.*, 1927, 3015): the corresponding chloride was synthesised. As carajurin affords *p*-acetylanisole on degradation by alkalis, the only dubiety concerns the position of one methoxyl, and the formulæ (XXXI) and (XXXII) are the alternatives. The red colour of the quinonoid colour base excludes the *o*-quinonoid structure (which by analogy would be associated with a violet or blue colour). Of these formulæ, (XXXI) is the more probable because the ferric reaction of carajurin salts suggests that two hydroxyls are in the *o*-position.



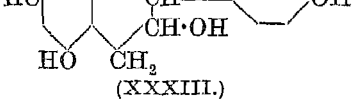
(XXXI.)



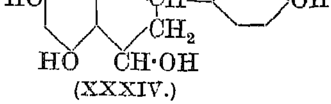
(XXXII.)

The form in which carajurin occurs in the plant is unknown, but from the method of isolation it must be as a saccharide of some kind. The substance may be regarded as a fission product of an anthocyanin. In parenthesis it may be remarked that the possibility exists that carajurin may be a derivative of 5 : 7 : 8 : 4′-tetrahydroxyflavenol, because opening and closing of the pyran ring in the course of the demethylation cannot be excluded in the absence of synthetical evidence.

The idea that catechin should be regarded as a reduction product of quercetin was first advanced by Perkin (*J.*, 1905, **87**, 398; cf. Perkin and Yoshitake, *J.*, 1902, **81**, 1162). By oxidising catechin tetramethyl ether, he obtained veratric acid and, probably, phloroglucinol dimethyl ether. Hence the alternatives (XXXIII) and (XXXIV) were advanced.



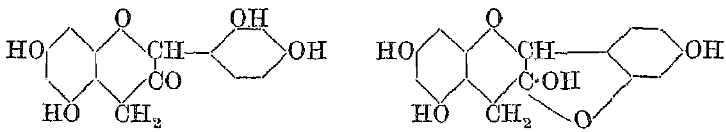
(XXXIII.)



(XXXIV.)

Acacatechin from *Acacia catechu* was proved to be an isomeride of catechin; it was subsequently shown by Freudenberg to be a mixture of *dl*-catechin and a little *l*-epicatechin. The same author showed that the catechins are stereoisomerides having the constitution (XXXIII).

Perkin made many further researches, such as those on scoparin (1899, 1900), vitexin, and homovitexin (1898, 1900), fukugetin (1904), excoecarin and jacarandin (1902), carthamin (1910), santalin and deoxysantalin (1918), acertannin (1922), which were largely descriptive, and the last substance to be mentioned in this section in more detail is cyanomaclurin, which he isolated from Jak-wood (*Artocarpus integrifolia*) (Perkin and Cope, *J.*, 1895, **67**, 937; 1905, **87**, 715). This interesting substance is a kind of catechin related to morin rather than to quercetin and it contains two hydrogen atoms less than catechin. Perkin showed that it may be degraded to β-resorcylic acid and phloroglucinol and suggested the formula (XXXV). It was later found that the deep blue colour produced on warming an alkaline solution of cyanomaclurin (hence the name) is due to the formation of the colour base salts of morinidin, and this confirms Perkin's hypothesis in essential respects. The slight modification (XXXVI) remains for consideration.



(XXXV.) (XXXVI.)

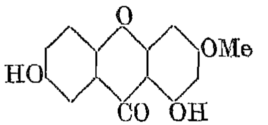
Other Natural Colouring Matters.

It is curious that Perkin took so little interest in plant colouring matters devoid of tinctorial properties, his sole contact with the carotenoids having been to show that the pigment of the Indian mahogany tree (*J.*, 1912, **101**, 1538) is identical with nyctanthin, later found (Kuhn and Winterstein, 1929) to be identical with crocetin. He found several new sources of berberine (Perkin and Hummel, *J.*, 1895, **67**, 414; Perkin, *J.*, 1897, **71**, 1198).

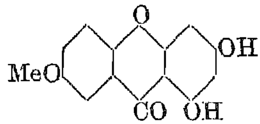
In connection with natural indigo he made more extensive researches (Perkin and Bloxam, *J.*, 1907, **91**, 279, 1715; 1910, **97**, 1460; Perkin and Thomas, *J.*, 1909, **95**, 793; Perkin, Thomas, and Bloxam, *ibid.*, p. 824; Perkin, *ibid.*, p. 847), the most important outcome being the method devised for the analysis of the indican

content of the leaves of the indigo plant. The estimation depended on the formation of indirubin by the acid hydrolysis of the indican in a neutral atmosphere in presence of isatin. Indigo-yellow from the Java indigo plant (*Indigofera arrecta*) was shown to be kæmpferitrin, a rhamnoside of kæmpferol (*J.*, 1907, **91**, 435).

Degradative evidence leaves two possible formulæ for gentisin, namely, (XXXVII) and (XXXVIII), and, as a result of the study of the properties of bisbenzeneazogentisin, Perkin was led to prefer the former.



(XXXVII.)



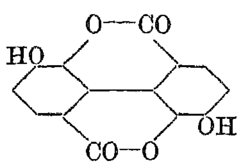
(XXXVIII.)

The correctness of this conclusion was later demonstrated by a synthesis of a substance corresponding to the alternative expression (Shinoda, *J.*, 1927, 1983).

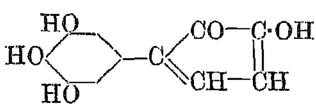
Although not strictly relevant, the opportunity may be taken here to mention the preparation of some analogues of ellagic acid by the oxidation of hydroxy-derivatives of benzoic acid.

For example, catellagic acid (XXXIX) was obtained from protocatechuic acid by oxidation with potassium persulphate and sulphuric acid. The oxidations were occasionally carried out electrolytically (Perkin and Nierenstein, *J.*, 1905, **87**, 1417; Perkin, *J.*, 1906, **89**, 251; A. G. Perkin and F. M. Perkin, *J.*, 1908, **93**, 1194; Bleuler and Perkin, *J.*, 1916, **109**, 629).

Related to this topic is the work which Perkin carried out on purpurogallin, the constitution of which (XL) was eventually established by Willstätter and Heiss (*Annalen*, 1923, **433**, 17). In



(XXXIX.)



(XL.)

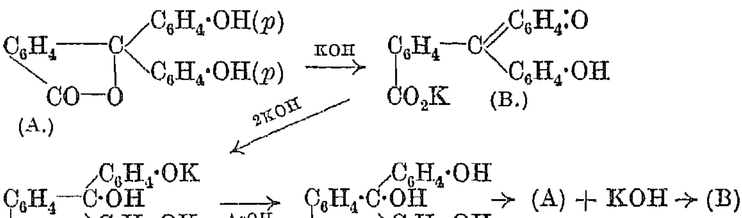
collaboration with F. M. Perkin it was noted that purpurogallin could be obtained by the anodic oxidation of pyrogallol (*J.*, 1904, **85**, 243), but for the preparation of the substance Perkin and Steven (*J.*, 1903, **83**, 192) preferred the nitrous acid process of Nietzki;

ferricyanide also was found to be applicable. The older formulæ, for example, $C_{20}H_{16}O_9$, were shown to be incorrect and were replaced by the formula $C_{11}H_8O_5$. Various derivatives (*e.g.*, tetra-acetate, dibromo-tetra-acetate, monopotassium salt, purpurogallone derivatives, and *iso*purpurogallone) were prepared and the formation of naphthalene by zinc dust distillation was confirmed. This proved a confusing factor, but Perkin suggested that one of the hydroxyl groups is in a side chain and he detected the presence of a carboxyl group in purpurogallone.

Work in Collaboration with Professor A. G. Green.

Some new polythiosulphonic acids of *p*-diamines were oxidised in the presence of aromatic amines and the products were shown to differ from known colouring matters of the sulphur class (*J.*, 1903, **83**, 1201). A note on the constitution of cellulose was published in 1906. The behaviour of phenolphthalein and quinolphthalein was studied with highly interesting results (*J.*, 1904, **85**, 398).

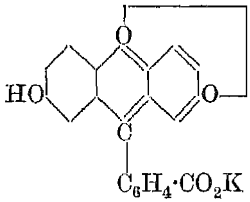
The first product of the action of alkali on phenolphthalein is the red quinonoid salt in which the lactone ring is broken. Then with more concentrated sodium hydroxide the quinone is hydrated and a colourless solution is obtained. Cautious neutralisation with acetic acid gives the free phenolic carbinol in which the carboxyl group alone is present in salt form. On heating, the lactone is probably regenerated with liberation of alkali-metal hydroxide (or the quinonoid phase is directly produced by dehydration). These changes are represented as follows :



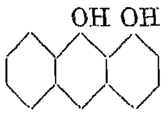
It was possible to follow these stages in the case of quinolphthalein and the formula (XLI) was suggested for the colour salt in this case. The hypothesis was analogous to the proposals of Kehrmann in connection with the constitutions of members of the rosindone and oxazine groups.

Reduction Products of Hydroxyanthraquinones.

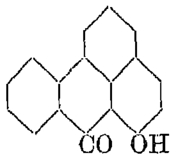
A long series of researches on this subject was Perkin's last interest and constitutes his major contribution to synthetic chemistry. Fourteen papers in this series were published between 1922 and 1933. It was found that the reduction of unsymmetrical hydroxyanthraquinones leads, as a general rule, to only one of the two anthranols which might theoretically be obtained. Thus 1-hydroxyanthraquinone gives (XLII) because the hydroxyl group of the corresponding benzanthrone (XLIII) is resistant to methylation by means of methyl iodide and alcoholic potassium hydroxide.



(XLI.)



(XLII.)



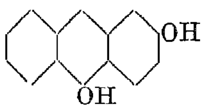
(XLIII.)

In a similar manner the constitutions of the anthranols (anthrones) from alizarin and its 2-methyl ether, anthrapurpurin, flavopurpurin, anthragallol and its methyl ethers, were determined (*J.*, 1920, **117**, 696; Perkin and Spencer, *J.*, 1922, **121**, 474; Perkin and Miller, *J.*, 1925, **127**, 2684; Perkin and Cross, *J.*, 1927, 1297; 1930, 292).

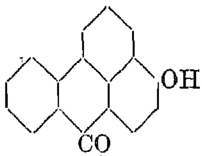
In the 1-hydroxyanthraquinones it was found that the carbonyl in the *o*-position to hydroxyl is protected from the action of the reducing agent, but if this hydroxyl is acetylated, then the carbonyl ortho to acetoxyl is the one attacked. Thus the isomeric anthranols could be obtained at will.

The reduction of 2-hydroxyanthraquinone was found to give 3-hydroxyanthranol (XLIV), and therefore a *p*-hydroxyl also protects a carbonyl from reduction. The corresponding hydroxybenzanthrone (XLV) was obtained also by the direct oxidation of benzanthrone by means of aqueous potassium hydroxide and some potassium chlorate at 230—240°, and its methyl ether afforded 2-methoxyanthraquinone-1-carboxylic acid (XLVI) on oxidation by means of chromic acid (Perkin and Spencer, *loc. cit.*; Perkin and Bradshaw, *J.*, 1922, **121**, 911; misprinted 1911 in *J.*, 1924, **125**, 231). The dianthracene derivatives from 2-hydroxyanthraquinone were studied in very great detail and the results are of considerable scientific

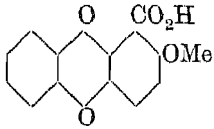
and technical interest. Perkin and Bradshaw treated 2-hydroxy-anthraquinone with glucose, aqueous alkali, and potassium nitrate at 170—180° and obtained 2-hydroxybenzanthronecarboxylic acid together with substances at first considered to be $C_{28}H_{16}O_4$ (A) and $C_{28}H_{14}O_4$ (B). Perkin and Whattam (*J.*, 1922, **121**, 289) reduced 2-hydroxyanthraquinone by means of zinc dust and ammonia to 3-hydroxyanthranol (XLIV) and obtained as by-products 2 : 2′-dihydroxydianthryl and 3 : 3′-dihydroxydianthrone. The latter on oxidation with permanganate gave a supposed dihydroxydianthraquinone identical with the product (A) of Perkin and Bradshaw.



(XLIV.)

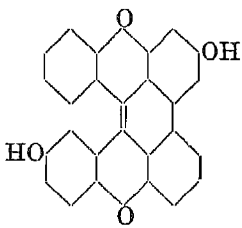


(XLV.)

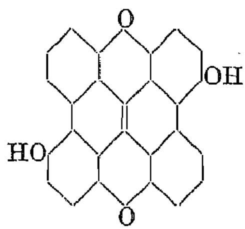


(XLVI.)

Later, Haller and Perkin (*J.*, 1924, **125**, 231) oxidised dihydroxydianthrone with ferricyanide and obtained a 99% yield of (A) $C_{28}H_{14}O_4$, and a trace of (B). Because (A) is converted by iodine in pyridine solution into a monoiodo-derivative without further nuclear coupling, it was regarded as 3 : 6′-dihydroxyhelianthrone (XLVII). (B) was now recognised as $C_{28}H_{13}O_4$ and formulated as a dihydroxy*meso*naphthadianthrone (XLVIII).



(XLVII.)



(XLVIII.)

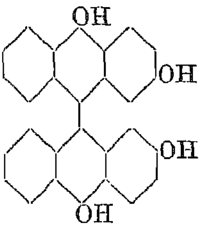
The dihydroxyhelianthrone gives orange-red alkali salts and a bluish-green vat in which fibres are dyed bluish-green, becoming red and then orange on exposure to air.

In later researches these conclusions were modified (Perkin and Yoda, *J.*, 1925, **127**, 1884; Perkin and Hardacre, *J.*, 1929, 180) and it was shown that on mild oxidation 3-hydroxyanthranol gives successively 3 : 3′-dihydroxydianthrone (XLIX), dihydroxydi-

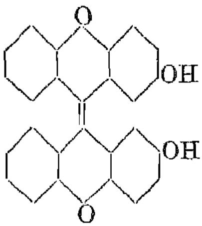
anthraquinone, dihydroxyhelianthrone (LI), and dihydroxynaphthadianthrone (LII).

The position of the hydroxyl groups was proved by synthesis (Perkin and Hardacre, *loc. cit.*). 1-Bromo-2-benzoyloxyanthraquinone was treated with copper powder according to Ullmann's method and after hydrolysis 2 : 2′-dihydroxy-1 : 1′-dianthraquinonyl (LIII) was obtained. This was reduced to dihydroxydianthranolyl (LIV) and then oxidised to the dihydroxyhelianthrone (LI).

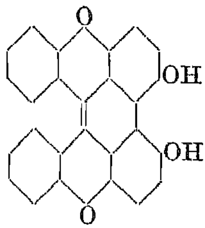
Somewhat different results were obtained by the oxidation of the anthranol (LV) from alizarin 2-methyl ether (Perkin and Attree, *J.*, 1931, 144; Perkin and, in part, Haddock, *J.*, 1933, 1512).



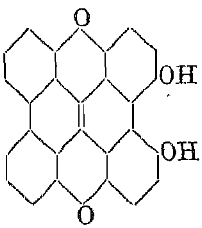
(XLIX.)



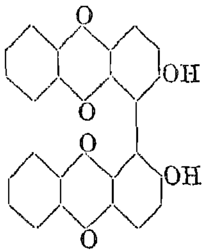
(L.)



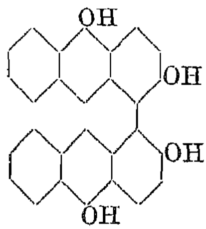
(LI.)



(LII.)



(LIII.)

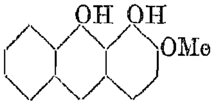


(LIV.)

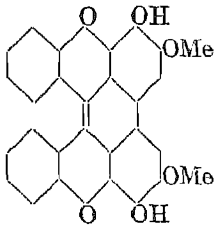
When iodine in pyridine solution was used as the oxidising agent, the product obtained was at first thought to be a dihydroxydimethoxyhelianthrone (LVI) analogous to that obtained from 2-hydroxyanthraquinone. This substance was, however, synthesised, and proved to be a different compound. The oxidation product of the anthranol (also obtained by boiling a pyridine solution of 4-bromo-1-hydroxy-2-methoxyanthrone) was recognised as a dihydroxydimethoxydibenzperylenequinone (LVII).

The last piece of work which engaged Perkin's attention showed that his powers as a discoverer were unimpaired. In attempting

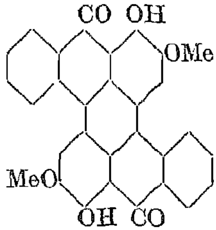
the methylation of 3 : 4-dihydroxyanthranol by means of methyl sulphate and anhydrous sodium carbonate in crude trichlorobenzene solution, the formation of a green vat-dye was observed. Further investigation showed that the presence of tetrachlorothiophen in the trichlorobenzene was responsible for the production of this interesting substance, and related products were obtained from 4-hydroxy-3-



(LV.)



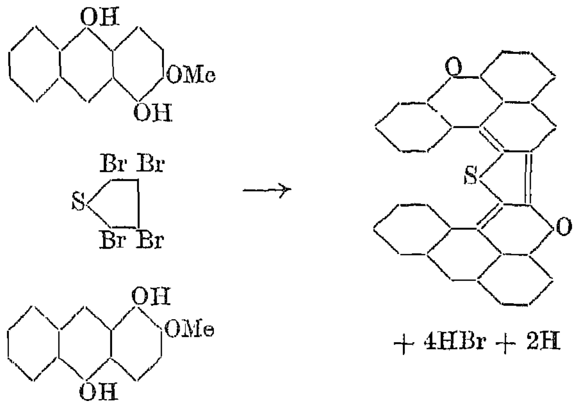
(LVI.)



(LVII.)

methylanthranol and from 4-hydroxy-3-methoxyanthranol (cf. B.P. 353,422, Imperial Chemical Industries Ltd., A. G. Perkin, A. Shepherdson, and N. H. Haddock). The dyes applied to cotton from a hyposulphite vat yield green shades of considerable beauty but of only moderate fastness to light and hypochlorite; they may nevertheless be of technical interest.

In a posthumous paper (Perkin and Haddock, *J.*, 1938, 541) it is shown that the dyes can be oxidised by chromic acid with formation of the anthraquinone corresponding to the anthranol employed. The formation of the dye from the 4-hydroxy-3-methoxyanthranol is represented as follows :



Perkin was a very great chemist and a man of characteristic and lovable personality. His gentle, unassuming, and to a certain extent, retiring nature prevented him from taking a large part in national scientific affairs, but his laboratory activities gave him an international reputation second to none as an ardent and successful seeker of the truth. He was an ideal colleague, completely unselfish, a giver not a taker, a man who craved no recognition and sought no reward other than the joy of accomplishment.

[*Reproduced by permission of the Royal Society.*

A. G. GREEN

ARTHUR GEORGE GREEN

1864—1941

ARTHUR GEORGE GREEN died peacefully in his sleep on September 12th, 1941, in the seventy-eighth year of his life. From leaving college in 1885 until the day of his death Green was continuously and actively engaged in the practice of chemistry. He was preeminently a chemist; all his enthusiasm, and it abounded in him, was for chemistry or for causes which had chemistry at the heart of them. The synthetic dyestuff industry was his foremost passion and practically all the energy of his long life was devoted to it, not merely because he had fertilised it by his early genius as an inventor, or because it furnished an outlet for his talent as an experimenter, but because he believed in it fervently as a matter of major significance in the industrial and scientific development of the nation. The dyestuff industry was a " cause " to Green. He was a servant to science, and a passionate preacher of science in industry. He was properly honoured for his work and for his devotion by his colleagues, becoming a Fellow of the Royal Society and the recipient of many honours, medals, etc., from other learned bodies. From the politician and the general public, however, Green received no recognition. On this account, and because of the intensity of his belief in the urgency of his cause, Green must have experienced many times the pangs of disappointment and frustration, but in spite of it, and of the many changes in his career, his life was happy and uninterrupted in the steady and fruitful practice of the branch of chemistry of which he was a master. To have been able to do this up to the very day of his death was his greatest reward.

Green commenced his life work in dyestuff chemistry while it was still comparatively young, both as a branch of science and as an industry. Very early in his career, he blossomed out as an inventor and ranks amongst the select band whose discoveries ensured the establishment of the great industry of synthetic organic chemicals of which the artificial colouring matters have always been the pivot and the inspiration. He suffered the chagrin of seeing the industry

which had been born in this country come to its fullest fruition in another land, then in the last period of his life he saw it flourishing once more in the land of its birth.* At the end of his life Green passed his happiest days amongst the new generation of colour chemists who arrived on the British scene with the renaissance of the industry on which he had set his heart.

Green was born a Londoner, the son of an architect, and was educated at Lancing College, Sussex. He confessed himself to have been an indifferent pupil until he was allowed to work in the almost unused chemical laboratory of the school during play hours. After matriculating, in 1880, he entered University College, London, where he studied chemistry under Williamson, physics under Oliver Lodge, and biology under Ray Lankester. At the end of his first year, he gained a gold medal and a Clothworkers' Exhibition in chemistry, and the seal was set on his career. More medals, a Tuffnell Scholarship and research work with Dr. H. F. Morley followed. During college vacations Green had worked as a volunteer in the laboratory of Messrs. Williams Bros., aniline dye manufacturers of Hounslow. He introduced to the firm the "baking" process for the manufacture of sulphanilic acid, and throughout his career, with breaks from time to time, he maintained his old connection with this ancient firm.

Green was by this time completely committed to dyestuff chemistry, and when he left College in 1885 obtained his first post as research chemist to the firm of Messrs. Brooke, Simpson & Spiller, Ltd., Atlas Works, Hackney Wick, where, incidentally, he succeeded Meldola, who was leaving to become professor of chemistry at Finsbury Technical College. While in the service of this firm Green made his first dyestuff inventions. These were of outstanding merit and included primuline, which was not only a new dyestuff but led Green to uncover an entirely new technique in the application of dyestuffs on cotton. In the light of later knowledge it is easy to see that Green's inventions at this early stage of his career could and should have built up the fortunes of a dyestuff business in this country comparable with the powerful firms which were developing in Germany. This was not to be, however, and Green, mortified at the want of appreciation of these wonderful possibilities, transferred his services in 1894 to the Clayton Aniline Company in Manchester.

* Compare the two lectures: (*a*) The Relative Progress of the Coal Tar Industry in England and Germany during the past Fifteen Years (*J. Soc. Dyers and Col.*, 1901, **17**, 285); (*b*) "The Renaissance of the British Dyestuff Industry" (*ibid.*, 1930, **46**, 341).

From 1894 to 1901, Green laboured at Clayton as research chemist and works manager. His earlier inventions in the primuline field were developed and greatly improved, and progress was made in other classes of dyestuffs, notably the derivatives of stilbene. Under Green's regime the Clayton works was greatly enlarged, and in addition to his many patented inventions during this period, and some publications in scientific journals, Green participated in the development of a modern manufacturing technique. A case in point was the establishment on a large scale of the manufacture of *p*-nitroaniline by the acetanilide route, using an aluminium reaction vessel with a silver condenser, great innovations in their day.

At the turn of the century the position of the dyestuff industry in England was critical. Green's inventions and the position he occupied augured possibilities which could be compared with what Caro, for example, had done for German industry. The manufacture of dyestuffs was already emerging from its earliest, or " rosaniline " period when Green commenced his career. In those early days it could only be reckoned as a small sundries type of industry. Now, however, owing to the progress of the azo dyes under Caro's presiding genius, and the consequent demand for intermediates on a bulk scale, a complete change had come about. The improvised technique and the elementary conceptions of plant, borrowed for the most part from other trades, which had characterised the early phase of the industry now no longer sufficed. The manufacture as well as the chemistry of dyestuffs had become scientific, and a new phase was inaugurated by the production of synthetic indigo on the large scale. The latter event saw even inorganic processes such as electrolytic alkali and chlorine, as well as contact sulphuric acid, invented and developed solely in order to meet the need of the dyestuff industry to obtain its primary products on a bigger and more economic scale. With these developments the German dyestuff firms progressed from strength to strength, a fact of which Green was keenly aware, and which caused him to despair as he came to realise his failure to arouse interest among the industrial and political leaders of this country. It is not surprising, therefore, that at this stage Green severed his connection with industry. He left the Clayton Aniline Company in 1901.

Green's next venture was to open a private laboratory in London in order to sell his ideas and to act as a chemical consultant. Within a short time, however, he was invited to accept the chair of Colour

Chemistry and Dyeing at the University of Leeds (at that time the Yorkshire College, a constituent of the Victoria University).

Green's appointment as professor, direct from industry and without any academic experience or standing, reflects considerable credit on the enterprise and judgment of those responsible at Leeds. He was, however, well fitted for the post and, although he had a most distinguished predecessor in the late Professor Hummel, Green, during the period 1903—16, in which he occupied the chair, greatly enhanced the reputation of his department, both in teaching and in research.

Liberally endowed by the Clothworkers' Company, according to the standards of the day, Green's department at Leeds became not only an outstanding example of the teaching of applied science, but it acquired an international reputation for its research work. Graduates of universities, both in this country and abroad, came to work under Green, and the students of the department were eagerly sought after, even by the great German dyestuff firms.

The nature and the success of Green's work while in the chair at Leeds are well indicated in his original publications during this period. These are almost exclusively of a scientific character, but he never entirely lost his contact with the dyestuff industry at home and abroad, with which he had many consulting connections. As the discoverer of a new method of dyeing Aniline Black he also had a very intimate practical contact with the dyeing trade through the grant of patent licences in many countries.

By a coincidence, one of Green's contemporaries at Leeds was Procter, head of the Department of Leather Technology. Procter, too, had been recruited from industry and had an international reputation, not only for the training of students in the scientific aspects of industry, but also for his pioneer work in colloid science. The importance of the teaching and the original work done by men of the type of Green and Procter in the interest of the scientific development of industry is usually insufficiently appreciated by those in authority over matters educational. The faintly acidulous attitude too often shown by the academic world towards the more "applied" aspects of advanced scientific education was not absent at Leeds; perhaps the lessons now brought home so painfully by a technical war were not so obvious in 1914. Whatever the reasons Green was restless at the time and when war broke out was probably feeling a strong urge to get back into industry.

The war in 1914 brought new ideas and responsibilities to Green. All his forebodings and warnings about the decadence of organic chemical industry in England proved to be only too well founded when, out of our unpreparedness, we had to improvise the means to deal with a scientifically well-equipped foe. Like other academic leaders in chemistry Green was faced with the need of finding men for the understaffed factories and of assisting the Government with advice and hurriedly improvised research work. Green's experience in the dyestuffs field led him to useful contributions in many directions; for example, in the explosives field he pioneered the chlorodinitrobenzene route to picric acid (B.P. 16,607, 1915).

The dyestuff crisis was one of the most acute of the many technical problems with which the country was faced at this time. Not only was there an insufficiency of plant and experience to meet more than a small fraction of the urgent demand, but, owing to the comparative neglect of scientific research and advanced teaching in organic chemistry at the universities, there was an insufficiency of men of the type required for the hurried improvisation of an entire industry, which was what the situation called for. In this chaos Green resigned his chair at Leeds early in 1916, and took on the double responsibility of establishing the Dyestuffs Research Laboratory at the Manchester College of Technology, and at the same time acting as adviser to the firm of Levinstein, Ltd., who were at that time bearing the brunt of the increased dyestuffs production. An outstanding event in Green's connection with this firm was his collaboration in the working out and establishment of the technical production of "mustard gas" on the large scale.

Green's interest did not wander from dyestuffs for very long, and the end of the war found him working whole time with Levinstein, Ltd., as director of a new research laboratory staffed very largely from the pick of the chemists released from other fields of the war effort. Green held this appointment through the troubled times which fell upon the dyestuff industry in the early years of peace. The struggling industry was the subject of much political controversy as well as many changes in management resulting from the "rationalisation" which was part of the post-war economy, and on top of this it was all but ruined by the effects of the Sankey judgment.

In 1923, Green's firm, having in the meantime become the British Dyestuffs Corporation, Ltd., lost his services on account of a disagreement on policy. Green held the view that an industry de-

pendent on scientific development should be in the hands of men having the fullest appreciation of science, that is to say, of scientists. This view was not commonly held by his contemporaries, but Green knew only too well from personal experience the disaster which the industry had suffered in this country through falling into the hands of men who lacked knowledge, and he was anxious that the mistake should not be repeated. Unfortunately he chose the wrong moment to attack, pressed his point, and lost; had he waited, he would have been successful, judging in the light of subsequent events in the industry. It is safe to say, however, that in the period during which Green directed his laboratory at Blackley the seed was sown for the great revival of the dyestuff industry which followed there later. The reason for this was the fact that wherever Green established himself his efforts were always directed along the path of originality and discovery, as the true object of research. When his old firm found itself in circumstances of greater security under the ægis of Imperial Chemical Industries, Limited, it blossomed out in an ambitious and successful research effort which commanded the respect of the world of chemical industry and secured it many commercial advantages. This success can safely be attributed to the inspiration gained in many ways, direct and indirect, from the inventive spirit of A. G. Green.

During his period at Blackley, Green's interests covered a wide field of dyestuffs invention and he revived an old attachment he had always had for the chemistry of synthetic drugs. The close connection between drugs and dyes is well known, and it is significant that the continental dyestuff manufacturers have been responsible for some of the world's greatest advances in chemotherapy. It was natural, then, that Green should concern himself with this off-shoot of the dyestuff industry and in his later years his "retirement" was largely devoted to experimental work on the subject in his private laboratory. This work bore fruit in the issue on the market of sulphanilamide EOS, a useful contribution to chemotherapy, shortly after Green's death (Green and Coplans, B.P. 524,011; *idem, Chem. and Ind.*, 1940, 59, 793).

Green resumed his connection with his old colleagues in the dyestuffs industry at Blackley during the last six years of his life, when he became a consultant to Imperial Chemical Industries, Ltd., and, by his regular visits to the great laboratories which the firm had built at Blackley, was able to participate in and inspire the work of the new generation of dyestuff chemists. It was a unique oppor-

tunity for these younger men to learn from one of the early pioneers of the industry that in spite of the enormous strides which had been made on the theoretical side of chemistry in the intervening generations, and the colossal amount of publishing and patenting which had filled in the years, old Nature's lap is still full of prizes for those who will acquire the knack of putting the right kind of questions to her. To quote a Chinese proverb, " To ask well is to know much." Green was very successful in imparting the art of " asking," and his pupils have played a considerable part in the restoration of the dyestuffs industry in this country.

In personal disposition Green's character was of the mildest and gentlest. His fervent belief in science as a keynote in modern life, and in the dyestuffs industry as a keystone in modern industrial development, was never expressed in mere pugnacity, but rather as a quest, a persistent crusade for that in which he believed with all his heart. Nevertheless there was plenty of toughness of moral fibre in Green, and through the varying phases of his career, he never once surrendered the ideals for which he had battled all his life.

Green's work earned him many honours in the worlds of science and technology. These included election to the Royal Society (1915) and the honorary degree of M.Sc. of the University of Leeds (1905). He was the recipient of the Perkin Medal in 1917. He was very proud to be made a Liveryman of the Worshipful Company of Dyers (1918) and on three occasions he was awarded the Company's Gold Medal. He was an Honorary Member of the Society of Dyers and Colourists, and President in its Jubilee Year. He was elected a Fellow of the Chemical Society in 1885.

Apart from chemistry Green had few interests. He liked foreign languages and travel, and in his early days tramped and cycled extensively in continental countries. He had a happy family life and his character was seen best in this setting—a simple man whose ambition was all for his science.

Green's domestic life was one of unclouded happiness until he lost his wife early in 1941. She was the daughter of Henry Charles Heath, a well-known miniature painter. For fifty-two years she supported him in his many struggles and vicissitudes and nursed him through several serious illnesses, for, though apparently as wiry in body as in spirit, Green's health was never robust. She gave him two daughters, and amongst his private papers he left a most touching

tribute to her brave spirit. There is no doubt that the shock of her death hastened his own end, for he followed her within a few months.

In attempting to appraise Green's life-work, one must place his merit as an inventor in the forefront. The outset of his career was signalled by a dyestuff invention which stands out in the history of that industry. Green was also a successful teacher, and, during his academic period, he turned out a great volume of original scientific papers in collaboration with the numerous research students who were attracted to his Leeds laboratory. From the beginning to the very end of his career, however, Green never ceased to give his thoughts to industrial problems and inventions.

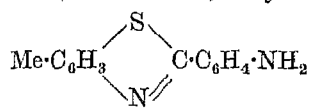
Green's career may be divided into three periods: the early-industrial up to about 1900, the middle-academic, interrupted by the war in 1916, and the post-war industrial and consulting period. Green's warwork was an interruption which deserves special mention. Comparison of these phases is not really possible, but, in my view, the first period was the most pregnant, and it was Green's tragedy (and ours) that its potentiality was not recognised and exploited effectively for the benefit of British industry. Green "arrived" just about the end of the early, or "rosaniline" period of the dyestuffs industry. He missed, therefore, being one of that band of the earliest pioneers who in the twenty years following the discovery of mauve made fortunes and retired young.* Instead Green found employers for his young talent who were completely lacking in knowledge of the science on which the industry rested and indeed without ordinary vision, since, apparently, they thought the industry was past its hey-day, an attitude which is almost unimaginable in the light of events and is, perhaps, another example of the curious kinks in Victorian mentality.

It is a matter of history that when Green came on the scene the dyestuff industry was just entering a new phase, when its real economic possibilities were to be clearly indicated by the rise of the azo dyes and eventually confirmed by the large-scale production of synthetic indigo. This was the psychological moment for "big business" to step in. Unfortunately for this country, however, organic chemistry lay beyond the vision of its business leaders; had it been otherwise Green would undoubtedly have given the impetus in this country which men like his contemporaries René

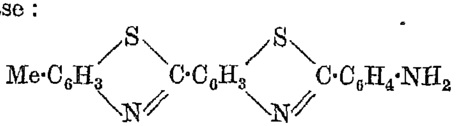
* Cronshaw, "In Quest of Colour," Society of Chemical Industry Memorial Lecture (*Chem. and Ind.*, 1935, **54**, 515, 547).

Bohn, T. Sandmeyer, and R. E. Schmidt gave on the continent, resulting in the establishment of dyestuff technology as a primary industrial power-centre from which radiated eventually many other branches of organic chemical industry, *e.g.*, drugs, artificial fibres, new photographic technique, and synthetic polymers, to say nothing of the consequent developments in inorganic chemicals which the new organic industry consumed in large quantities. The fruits of Green's inventions up to about 1900 could, if properly developed, and the profits "ploughed in" to produce an ever expanding research, have established an industry in the country comparable at least with that which grew up in Germany and Switzerland. British inventiveness had proved itself in the pioneer period of the dyestuffs industry following Perkin's discoveries; it has proved itself again in the renaissance which followed after the First World War. Green's tragedy was that his talent was not exploited in his hey-day, and it took a war to prove that his views on the importance of the dyestuff industry to this country were not overstated. In the dangerous time ahead of us we must see to it that the lessons provided by Green's career are not forgotten.

Green's earliest invention was, it so happened, his most outstanding one, the discovery of primuline in 1887 (*J. Soc. Dyers and Col.*, 1888, **4**, 39; 1917, **33**, 137; *J.*, 1889, **55**, 227). By the action of sulphur on *p*-toluidine, the thiazole, dehydrothiotoluidine,



is formed; this substance is not a dyestuff. Green, studying this reaction, discovered that a more complex base can be obtained by the use of more sulphur and a higher temperature. The new base when sulphonated gave a dyestuff having affinity for cotton, which is dyed a bright pure yellow without the aid of a mordant. The new dyestuff has been shown to consist substantially of a sulphonic acid of the base:



The derivation from *p*-toluidine is obvious; the position of the sulphonic group has not yet been proved.

The new dyestuff, although fugitive to light, was an attractive

addition to the, at that time, very limited range of direct dyeing cotton colours (Congo red, the first of the benzidine dyes, was less than three years old), but Green had still further work to do before primuline achieved the position it was later to assume as a major dye. Green applied his mind to the technique of dyeing and discovered the process of diazotising and developing on the fibre those substantive dyes which contain a reactive amino group. Primuline in this way gave a red with β-naphthol which achieved great industrial importance, and is still largely used though now past its hey-day on account of the discovery of faster modern "azoic" colours and other developed reds. Green's new dyeing process was as remarkable a piece of pioneering as the discovery of primuline itself (*J. Soc. Chem. Ind.*, 1888, 7, 179). Many inventors have over the years devoted their minds to the elaboration of direct cotton dyes suitable for diazotisation and development on the fibre, and the range of such dyes is to-day a large one. Invention in the series still goes on because, although every shade is now represented in the range, the production of certain developed shades, *i.e.*, yellows and greens, presents a problem which has a special challenge for the dyestuff chemist.

Besides the red obtained by diazotising and developing with β-naphthol, primuline gives other shades with other coupling components, *e.g.*, a bordeaux with ethyl-β-naphthylamine, a brown with *m*-phenylenediamine, etc. The diazo-compound is light-sensitive and has been employed in photographic reproduction, thus being the forerunner of the modern diazotype process which is now almost universally used for engineers' drawings (*J. Soc. Chem. Ind.*, 1890, **9**, 1001).

The "ingrain" process, as Green called it, of azo formation on the fibre not only had outstanding industrial importance but was a great piece of pioneering. The effect of increasing the molecular complexity of a substantive dyestuff on the fibre is not merely to modify the shade, but to increase the fastness of the dye. To-day this result is achieved in a number of analogous ways, and Green's invention must be regarded as the parent of the great range of "developed" colours, and in part at least, of the modern "azoic" colours. In the latter the process employed by Green is reversed, a coupling component which has a degree of affinity for cellulose, *e.g.*, β-hydroxynaphthoic anilide, being applied first and the diazo component afterwards. The fastness thus obtained is conditioned by the affinity of one of the components, a feature which is shared by

the original "ingrain" process of Green, and which distinguishes it from the older "para-red" process of Holliday. This development is mentioned here in order to emphasize the far-reaching effects of Green's early stroke of genius. Green's employers made the fatal mistake of not patenting primuline, and within a very short time it was successfully imitated by the Swiss firm of Geigy and later by every other dyestuff maker in the world.

The discovery of primuline led to many other new dyestuffs. A study of the action of ammonia on the diazo compound led to the discovery of a method of conferring cotton dyeing properties on the lower thiazoles derived from *p*-toluidine. These ideas were not patented or developed by Green's firm and dyestuffs arising from them were later manufactured by several other firms under the names of thiazol yellow, Clayton yellow, etc. A similar fate befell the valuable basic dyes discovered by Green when the bases obtained by the reaction of sulphur on *p*-toluidine are fully alkylated. A simultaneous discovery by the firm of Cassella led to the introduction of thioflavin T. Green's employers never took up the manufacture of this valuable dyestuff (*J. Soc. Dyers and Col.*, 1917, **33**, 139, 140). The discovery of primuline and its development created a whole chapter of dyestuff chemistry, competent exploitation of which could, in the judgment of well-placed observers in the German industry, have put the English firm in the front rank of the world's chemical manufacturers (*J. Soc. Dyers and Col.*, 1930, **46**, 341).

From now on, until he left industry in disgust, Green was occupied in a series of useful dyestuff inventions and their industrial development. Azo dyes and derivatives of dehydrothiotoluidine occupied most of his attention. This very substantial contribution to industry is, as usual, only sketchily described in the patents and occasional papers appearing in Green's name about this time. Some time after he became chief chemist and manager to the Clayton Aniline Company he took up the study of the stilbene dyes which was to occupy his interest, on and off, for a number of years. This class of dyestuffs is derived from *p*-nitrotoluene-*o*-sulphonic acid by treating it with alkali under various conditions. The first of the dyes which had been obtained by this reaction, known as sun yellow, or direct yellow A, was thought (Bender and Schultz) to be azoxystilbenedisulphonic acid :

$$\begin{array}{l}\mathrm{CH{\cdot}C_6H_3(SO_3H){\cdot}N} \\ \| \qquad\qquad\qquad\quad\;\; | \\ \mathrm{CH{\cdot}C_6H_3(SO_3H){\cdot}N}\end{array}\!\!>\!\mathrm{O}$$

This formula implies reducing conditions in the condensation. On further reduction a redder shade was obtained in which the azoxy group was supposed to be replaced by an azo group (Mikado orange), whereas under mildly oxidising conditions a greener shade of yellow was obtained (Mikado golden yellow). Green, studying these obscure reactions, discovered dinitrostilbenedisulphonic acid:

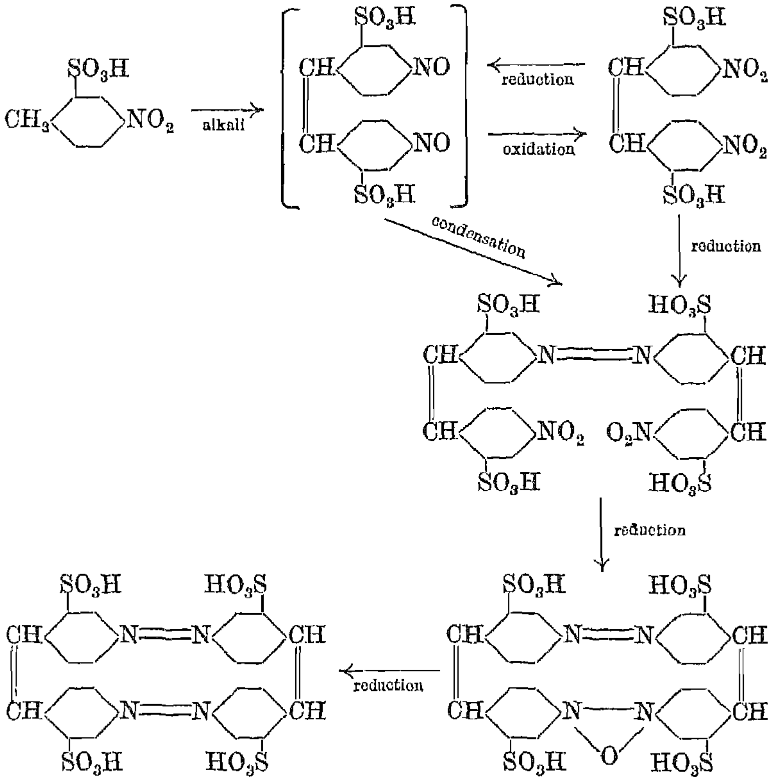
$$\begin{array}{l} CH\cdot C_6H_3(SO_3H)\cdot NO_2 \\ \| \\ CH\cdot C_6H_3(SO_3H)\cdot NO_2 \end{array}$$

to be the end product of oxidative condensation and from this starting-point he rationalised the preparation of the stilbene dyes. He manufactured them all from one starting-point, dinitrostilbenedisulphonic acid, by alkaline condensation under increasingly strong reducing conditions. In this way he obtained a series of dyestuffs, starting from a greenish yellow and gradually reddening to an orange, which issued under the trade name of stilbene yellows and oranges of various brands. This systematic procedure gave dyestuffs of improved brightness and purity and resulted in valuable business. The stilbenes, together with the thiazoles, still constitute the main bulk of the yellow direct cotton dyes. Remembering that Green had developed the thiazole series also at Clayton, it is not surprising that his company held an important position in this section of the dyestuffs field, a fact recognised jocularly at the time by references to Clayton's "Gelbsucht" (jaundice).

Green's interest in the stilbene class of dyes did not cease with the elaboration of manufacturing methods. He was not satisfied with earlier views on their constitution and began to work on the problem. This work was not completed, however, until ten years later, and is described in a series of papers * published from the Clothworkers' Research Laboratory at Leeds, in which it was finally established that the dyes obtained from *p*-nitrotoluenesulphonic acid were azo compounds, the azo group joining two stilbene residues in their *pp* positions; the *p'p'* positions being occupied by an azo-, an azoxy-, or nitro-groups, according to the degree of oxidation or reduction which had taken place during the alkaline condensation. The mechanism is shown on the scheme on p. 259, which postulates the transition formation of a nitrosostilbene, this being the cause of the

* Green (*J.*, 1904, **85**, 1424); Green, Marsden, and Scholefield (*J.*, 1904, **85**, 1433); Green and Crosland (*J.*, 1906, **89**, 1602); Green, Davis, and Horsfall (*J.*, 1907, **91**, 2076); Green and Baddiley (*J.*, 1908, **93**, 1721).

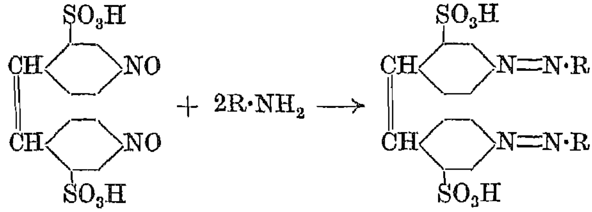
intense red to blue coloration observed initially when *p*-nitrotoluene derivatives are acted upon by alkali.



Further action of reducing agents results in the formation, first, of a leuco (hydrazo) compound, and, finally, of diaminostilbene-disulphonic acid. The above scheme over-simplifies the actual commercial processes, of course, since a mixture of products is usually obtained consisting not only of stilbene dyes containing a varying ratio of azo, azoxy, and nitro groups, but also dinitrodibenzyl derivatives (generally tending to be formed under conditions of milder alkalinity) and traces of azomethine derivatives and aldehydes

By his work on the constitution and mechanism of the formation of the stilbene dyes, Green paved the way to a further extension of

the series. He knew already in his Clayton days that dinitrostilbenedisulphonic acid could be condensed in alkaline solution with various amines to produce stilbeneazo dyes, the formation of which he later attributed to the reactive intermediate nitroso compounds, *e.g.*:



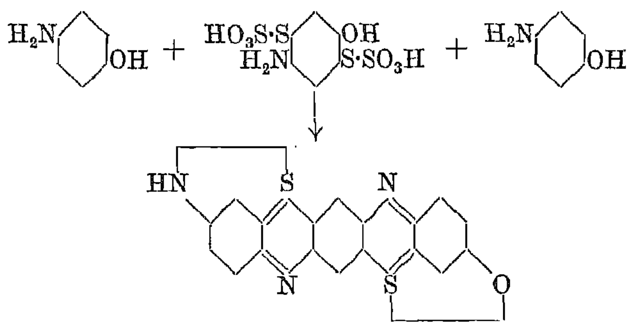
In all probability the products are mixtures, as in the case of the stilbene yellows.

The reaction was later extended by dyestuff manufacturers in several countries to include a wide variety of aminoazo compounds as reactive amines. This has resulted in a considerable number of valuable dyestuffs, chiefly browns, which constitute a major slice of that section of the direct cotton colour range.

Although developments in the thiazole and stilbene group of dyestuffs represent Green's main achievement in his Clayton period, he introduced a number of miscellaneous azo dyes, chiefly of the direct cotton series, *e.g.*, various rosophenine brands. There is, however, one other main topic to which he gave much attention, though without achieving the degree of success which attended his efforts in other fields.

The sulphide dyes, which had already attained some importance, during the last years of Green's stay at Clayton, reached the climax of their development with the arrival of the most important of them all, the famous black obtained by the thionation of 2 : 4-dinitrophenol. The chemistry of the sulphide dyes was unknown and their manufacture was (and still is) based on pure empiricism. Green thought that greater progress could be made if the constitution of the sulphide dyes could be ascertained and their synthesis thereby systematised. He attacked this formidable task, starting from Vidal's view that the sulphide blacks are polythiazines. He attempted a synthesis by making a dithiosulphonic acid of a *p*-phenylenediamine or of a *p*-aminophenol and oxidizing these together with amines, a scheme illustrated by the following example, in which the dithiosulphonic acid obtained by interaction of

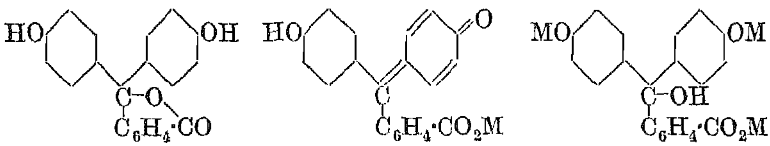
nitrosophenol and sodium thiosulphate in acid solution is brought into reaction first with two molecules of *p*-aminophenol :



This compound in the third phase of the reaction gave a sulphide dye (Green and Perkin, *J.*, 1903, **83**, 1201; Green and Meyenberg, B.PP. 21,832, 1898; 22,460, 1898; 22,847, 1898; 5039, 1899; 18,658, 1899; 4792, 1900). Along such lines several brands of Clayton fast blacks were made, which, on account of their freedom *from the by-products of the usual sulphide* "*melt*", *were* recommended as non-tendering and capable of use in calico printing (Green, *J. Soc. Dyers and Col.*, 1901, 17, 89; Green and Meyenberg, B.PP. 15,413, 1900; 15,414, 1900). These blacks were lacking in some other respects, however, and Green concluded, too, that the thiazine hypothesis did not apply to them, but that they were more analogous to aniline black in constitution, *i.e.*, were probably polyazines. The molecule is certainly complex, and depends for its dyeing properties not on its nuclear structure, but on the presence of –S–S– groups which, in the sulphide dye-bath, are reduced to –SH groups, which confer solubility. The soluble leuco compound is adsorbed by cellulose fibres, on which it reoxidizes to the insoluble –S–S– form and is then resistant to weak alkalis, acids, and to washing. No substantial advance has been made on these views of the chemistry of the sulphide blacks.

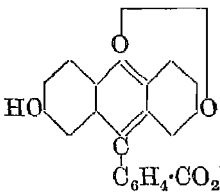
The only aspect of theoretical chemistry which interested Green to any extent was the quinonoid hypothesis as a convenient logical means of explaining the tinctorial properties and the chemical behaviour of dyestuffs, as well as many of the steps in their synthesis. He had been immensely attracted by Thiele's explanation of quinonoid addition and his theory of unsaturation and conjugation.

Green became a great advocate of these ideas in their application to dyestuffs, and they made his teaching lucid in a high degree (for an example of this see his paper on "Quinonoid addition as the mechanism of dyestuff formation", to the Eighth International Conference of Applied Chemistry). Various studies bearing on this topic are reported in several of his papers * extending over many years. His most challenging contribution was an attack on the textbook explanation † of the well known behaviour of phenolphthalein with alkalis (with A. G. Perkin, *J.*, 1904, **85**, 398). The physical chemists were inclined to the view, first advanced by Ostwald, that colour was the result of ionization, *i.e.*, the colourless acid of phenolphthalein forms salts, the ions of which are coloured. Green made the elucidation of the behaviour of the phthaleins a test case and the evidence of his experiments was accepted by Hantzsch as absolutely disproving the physical theory. Green's contention may be summarized thus: in phenolphthalein the coloured form has the quinonoid configuration (II), the original colourless acid and the colourless salt resulting from the action of excess alkali being represented by (I) and (III) respectively:



(I.) (II.) (III.)

This view of the *p*-quinonoid structure of phenolphthalein (coloured form) follows, of course, the ideas put forward to explain the structure of the triphenylmethane dyes by E. and O. Fischer and by Nietzki, *i.e.*, that they are *p*-quinonoid. In the case of quinolphthalein, for which a *p*-quinonoid formula cannot be written, Green postulated an *o*-quinonoid, oxonium, structure, *i.e.*:

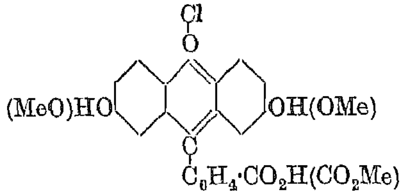


(coloured form)

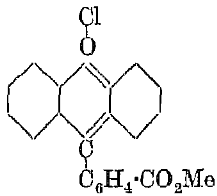
* *Proc.*, 1892, 195; *Proc.*, 1896, 226; *Ber.*, 1899, **32**, 3155; *Z. Farb. u. Textilchem.*, 1902, **1**, 413; (with F. M. Rowe) *J.*, 1913, **103**, 508.

† Ostwald, "Wissenschaftliche Grundlagen der Analytische Chemie."

These views found confirmation in the preparation and study of the ethers and esters of the phthaleins, and in the case of the quinol-phthalein the oxonium idea found striking support in the discovery of the series of coloured chlorides (Green and King, *Ber.*, 1906, **39**, 2365; 1907, **40**, 3724. See also *J. Soc. Chem. Ind.*, 1908, **27**, 4; 1909, **28**, 638):



Analogous oxonium chlorides (Green and King, *Ber.*, 1908, **41**, 3434) of the methyl esters of fluoran were also prepared in order to strengthen the cast still further, *e.g.*:



Green made important contributions on the subject of aniline black, on both the chemical and the technological side. Although one of the oldest of dyestuffs, having been observed by Runge in 1834, and having been in industrial use since 1862, its constitution and the mechanism of its formation were unknown. There had, moreover, been no substantial change in the commercial production of aniline black, which takes place on the fibre through the oxidation of aniline hydrochloride, generally with sodium chlorate and a copper salt in the presence of heat and moisture ("ageing"), finishing off with a sodium dichromate bath. Variations of the process consist in the replacement of the copper salt by a ferrocyanide or by a vanadium salt. All these methods require great care to avoid damage to the cotton fibre, which could arise from the presence of hydrochloric acid or oxides of chlorine which could be formed under the conditions of the process. Green endeavoured to mitigate these defects by replacing chlorate oxidation by air oxidation, using a small quantity of *p*-phenylenediamine in the presence of a copper salt as the oxygen carrying system. This process was patented (B.PP. 16,189, 1907;

19,129, 1912) and was successfully reduced to practice by Green and P. F. Crosland in several well-known Continental dye works.

Green speculated, of course, on the rôle of the *p*-phenylenediamine in the new process (*J. Soc. Dyers and Col.*, 1909, **25**, 188) and was led to study the mechanism of the formation of aniline black. He differentiated between "ungreenable" aniline black, which is the end stage of the dyeing process, and products then undergoing investigation at the hands of Willstätter and his school which these workers thought to be aniline black (*Ber.*, 1909, **42**, 2147, 4118; 1910, **43**, 2976; 1911, **44**, 2162), but which in Green's view, merely represented intermediate stages to the formation of the true black. This led to controversy (Green and Woodhead, *J.*, 1910, **97**, 2388; 1912, **101**, 1117; *Ber.*, 1912, **45**, 1955; Green and Wolff, *Proc.*, 1912, **28**, 250; *Ber.*, 1911, **44**, 2570; 1913, **46**, 33; Green and Johnson, *Proc.*, 1913, **29**, 276; *Ber.*, 1912, **45**, 33; 1913, **46**, 3769), but eventually the work of Green's school substantiated his views by identifying the products of the stepwise, *in vitro*, oxidation of aniline with the successive stages in the production of the commercial black and thus establishing a plausible rationale of the process.

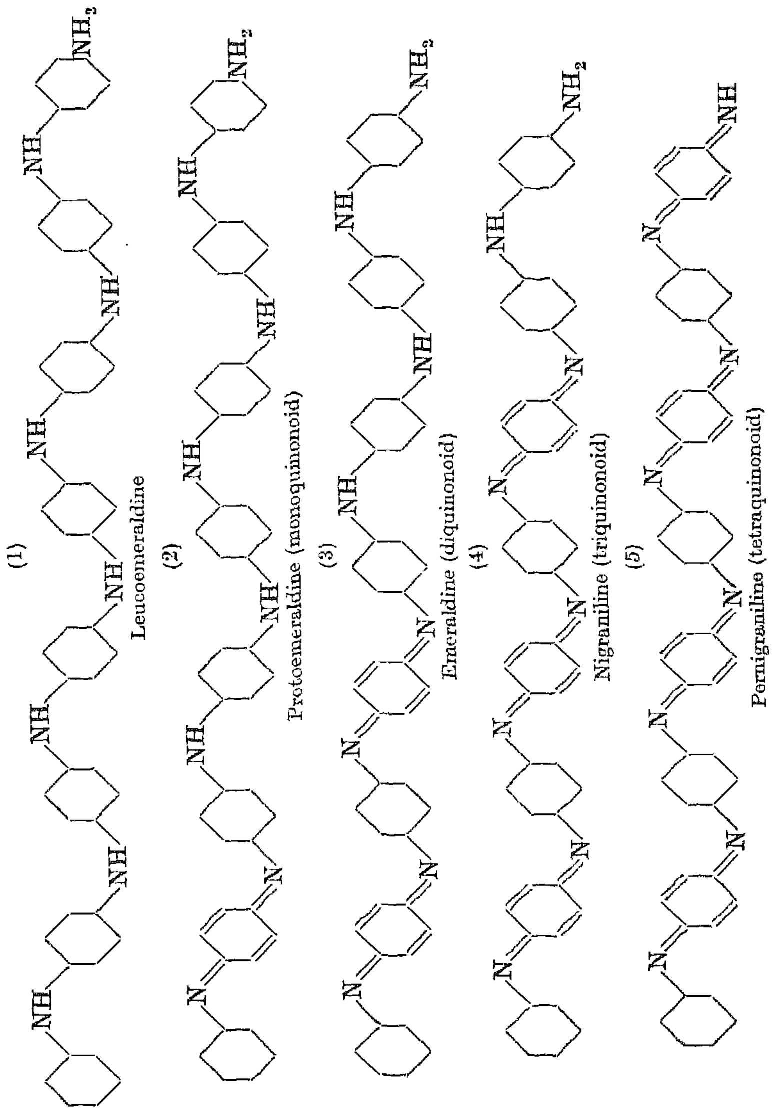
According to Green the first stage of the formation of aniline black consists in a series of oxidative additions of aniline to aniline in the manner of indamine formation (*i.e.*, linear) until eight aniline residues have been condensed.

Under carefully controlled conditions in the laboratory the products obtained from the oxidation of aniline salt by any of the commercial aniline black oxidation methods is either emeraldine or nigraniline, which substances are identical with the products well known to the aniline black dyer under these names. Emeraldine and nigraniline are merely oxidation stages of the same leuco compound which is the parent of all these substances, and also of two other oxidation stages which were discovered and named protoemeraldine and pernigraniline. The series is represented on p. 265.

Degradation results from more drastic action and the molecule breaks down to quinone as would be expected from its linear structure.

From his chemical work and technological observations Green was able to demonstrate that the final stage in the formation of aniline black is of an entirely different type from those which precede it, which are pictured above. Free aniline is involved and without it

the action cannot get beyond the nigraniline stage, *i.e.*, the ungreenable black cannot be formed. Neutral conditions are also necessary, such as in fact prevail in the last stage of the commercial process,



(1) Leucoemeraldine

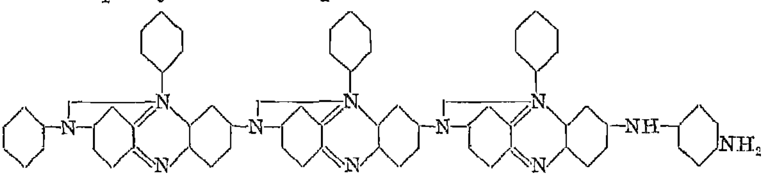
(2) Protoemeraldine (monoquinonoid)

(3) Emeraldine (diquinonoid)

(4) Nigraniline (triquinonoid)

(5) Pernigraniline (tetraquinonoid)

the bichromate treatment. In the laboratory such conditions give a product identical with the true aniline black and Green explained the formation of the latter in practice as being due to residual free aniline, still present on the cloth when it emerges from the ager and before it enters the dichromate bath. From these observations Green felt justified in concluding that the last phase in the aniline black process is an oxidative addition of further aniline with ring closure of the safranine type to give a salt (usually the chromate) of the triphenylazoniumoctaphenazine :



The conditions of the aniline black process are varied for commercial reasons and the degree of "ungreenability" attained depends on the completeness or otherwise of formation of the azine rings (Green and Wolff, *J. Soc. Dyers and Col.*, 1913, **29**, 105; see also Green and Johnson, *ibid.*, p. 338).

The similarity between the colour reactions of dinitrostilbene and of dinitroazobenzene, and the parallelism suggested by the formation of both substances by hypochlorite oxidations, thus :

$$\begin{array}{ccc} CH_3{\cdot}C_6H_4{\cdot}NO_2 & \qquad & NH_2{\cdot}C_6H_4{\cdot}NO_2 \\ \downarrow & & \downarrow \\ CH{\cdot}C_6H_4{\cdot}NO_2 & & N{\cdot}C_6H_4{\cdot}NO_2 \\ \| & & \| \\ CH{\cdot}C_6H_4{\cdot}NO_2 & & N{\cdot}C_6H_4{\cdot}NO_2 \end{array}$$

led Green to study the alkaline condensation of nitro-hydrazo compounds (Green and Bearder, *J.*, 1911, **99**, 1960; Green and Rowe, *J.*, 1912, **101**, 2003, 2443), with the object of finding further support for his views on the mechanism of the formation of stilbene dyes. Just as the unstable intermediate products (4 : 4′-dinitrosostilbenes) in the formation of stilbene dyes show a deep bluish-red to blue colour in alkaline solution, so also does the partial reduction product of 4 : 4′-dinitroazobenzene. In both cases the alkaline solutions are readily decolorised by air oxidation, the former yielding dinitrostilbene, the latter dinitroazobenzene. Green's work confirmed the product obtained by reducing 4 : 4′-dinitroazobenzene with ammonium sulphide to be dinitrohydrazobenzene. This dissolves in strong alkali with an intense blue colour and in

weak alkali with a violet blue colour. By acidifying the latter solution a compound was precipitated which, from analysis, appeared to be 4-nitro-4′-*nitrosohydrazobenzene*,

$$O_2N{\cdot}C_6H_4{\cdot}NH{\cdot}NH{\cdot}C_6H_4{\cdot}NO,$$

the coloured salts of which would have the quinonoid structure, $MO{\cdot}ON{:}C_6H_4{:}N{\cdot}N{:}C_6H_4{:}NOH$. While, therefore, the resemblance between the intermediate stages in the action of alkali on dinitrostilbene and on dinitroazobenzene is not complete, there is a striking analogy in the final product in the case of the dinitroazo compound, which yields bisnitrobenzeneazoazobenzene (dinitrotrisazobenzene):

$$\begin{array}{l} N{\cdot}C_6H_4{\cdot}N{=\!=\!=}N{\cdot}C_6H_4{\cdot}N \\ \| \qquad\qquad\qquad\qquad\quad \| \\ N{\cdot}C_6H_4{\cdot}NO_2 \quad O_2N{\cdot}C_6H_4{\cdot}N \end{array} \text{ (cf. Stilbene yellow)}$$

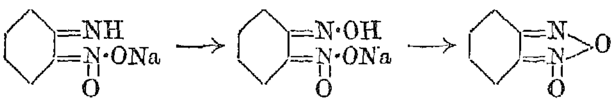
$$\begin{array}{l} CH{\cdot}C_6H_3(SO_3H){\cdot}N{=\!=\!=}N{\cdot}(HO_3S)C_6H_3{\cdot}CH \\ \| \qquad\qquad\qquad\qquad\qquad\qquad\quad \| \\ CH{\cdot}C_6H_3(SO_3H){\cdot}NO_2 \quad O_2N{\cdot}(HO_3S)C_6H_3{\cdot}CH \end{array}$$

On alkaline reduction tetrakisazobenzene was obtained,

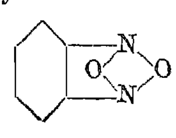
$$\begin{array}{l} N{\cdot}C_6H_4{\cdot}N{=}N{\cdot}C_6H_4{\cdot}N \\ \| \qquad\qquad\qquad\quad \| \\ N{\cdot}C_6H_4{\cdot}N{=}N{\cdot}C_6H_4{\cdot}N \end{array} \text{ (cf. Mikado orange)}$$

$$\begin{array}{l} CH{\cdot}C_6H_3(SO_3H){\cdot}N{=}N{\cdot}(HO_3S)C_6H_3{\cdot}CH \\ \| \qquad\qquad\qquad\qquad\qquad\quad \| \\ CH{\cdot}C_6H_3(SO_3H){\cdot}N{=}N{\cdot}(HO_3S)C_6H_3{\cdot}CH \end{array}$$

As the result of observations made during the course of the above work Green was led to investigate the oxidation products of *o*-nitroamines, the results of which are reported in a series of papers in collaboration with F. M. Rowe (Green and Rowe, *J.*, 1912, **101**, 2452; 1913, **103**, 508, 897; 1917, **111**, 613; 1918, **113**, 67, 2023; Green, B.P. 25,205, 1912). The behaviour of the nitroanilines with alkaline hypochlorite led Green to postulate the existence of quinonoid salts, of the nitronic acid type, *e.g.*, $C_6H_4{<}^{NH}_{NO_2Na}$, the reaction proceeding thus in the case of *o*-nitroaniline:



The resulting benz*iso*oxadiazole oxide (or benzfuroxan) was identical with the "dinitrosobenzene" of earlier literature. The constitution finally attributed was the symmetrical one:



because identical products were obtained from the pair of nitrotoluidines: $NH_2 : NO_2 : CH_3 = 1 : 2 : 5$ and $1 : 2 : 4$, and because of other supporting evidence.

Green's last published work in the dyestuffs field related to the so-called "sulphato dyes" and the "ionamines." The major bulk of textile dyeing is carried out in aqueous solution by means of dyestuffs which owe their solubility to the sulphonic acid group attached to an aromatic nucleus. (The sulphonation of rosaniline blue in 1862 by Nicholson was a crucial event in dyestuff history.) Green conceived the idea of solubilisation by means of an extra-nuclear sulphuric ester group and, in collaboration with Saunders, Adams, and Bate, made a series of new dyestuffs of the type

$$R{\cdot}NH{\cdot}CH_2{\cdot}CH_2{\cdot}O{\cdot}SO_3H$$

(R represents the rest of the chromophoric nucleus) which are conveniently and economically prepared by introducing the β-hydroxyethyl group into the dyestuff molecule (generally by reaction between an amino group and ethylene chlorohydrin), and then converting it to the sulphato compound by means of sulphuric acid (B.PP. 181,750, 182,031, 185,612, 186,878; Saunders, *J.*, 1922, 121, 2667; Green and Saunders, *J. Soc. Dyers and Col.*, 1923, **39**, 39). This invention put a useful new weapon into the hands of the dyestuff chemist.

The sulphonic acid group, which plays such a useful rôle in conferring solubility on dyestuffs, has the drawback of enabling the dyeing process to be reversed under certain conditions, *e.g.*, washing with soap or alkali. A further complication arises from the behaviour of the rayon made from acetylcellulose, which has no affinity for dyes containing the SO_3H group, and thus presented a formidable problem to the dyer when it first appeared on the market. Green overcame these difficulties by attaching to a dyestuff devoid of solubilising groups a methyl-ω-sulphonic acid group, a process easily brought about by condensing formaldehyde-bisulphite with an amino group attached to the dyestuff nucleus. Dyes of this type, *i.e.*, $R{\cdot}NH{\cdot}CH_2{\cdot}SO_3H$, are easily soluble in water in the form of their salts, but, on penetrating the fibre, dissociate with loss of formaldehyde and bisulphite, the residual dyestuff, now no longer soluble in water, being left firmly attached to the fibre. When the dyestuff residue indicated by R in the above formula is suitably chosen, useful products for the dyeing of cellulose acetate rayon are

obtained which appeared on the market under the name of "ionamines" (Green and Saunders, B.PP. 197,809, 200,873; Green, Saunders, and Frank, B.PP. 212,029, 212,030; Green and Saunders, *J. Soc. Dyers and Col.*, 1924, **40**, 138).

The above account of Green's experimental work covers the main topics which engaged his attention. Isolated researches * and the numerous lectures which he gave cannot be dealt with here, but the service he rendered to the dye technologist by his work on the identification of dyestuffs in substance and on the fibre should be recorded (Green, *J. Soc. Chem. Ind.*, 1893, **12**, 3; Green, Yeoman, and Jones, *J. Soc. Dyers and Col.*, 1905, **21**, 236; Green and Stephens, *ibid.*, 1907, **23**, 118; Green, Yeoman, Jones, Stephens, and Haley, *ibid.*, p. 252; Green and Frank, *ibid.*, 1910, **27**, 83). This work, extending over a number of years, was eventually published in book form. In spite of the volume of his writing on scientific, technological and economic matters, Green was only responsible for one other book, the *Systematic Survey of the Organic Colouring Matters*, adapted from Schultz and Julius's *Farbstofftabellen*, and incorporating a useful synopsis of information on the principal intermediates (published 1894).

To this career of endeavour and achievement the words of Thomas Browne are singularly appropriate:

> "Life is a pure flame and we live
> by an invisible fire within us."

Green's "pure flame" was his creative genius; his "invisible fire" was his extraordinary faith in the urgency of his cause. They sustained a comparatively frail body through a long life, full to the last of fruitful activity. He saw his cause triumphant in the end, though it required the ordeal of war to bring it home reluctantly to his countrymen.

* Examples are found in the following references: *Ber.*, 1893, **26**, 2772; (with A. G. Perkin) *J.*, 1906, **89**, 1811; (with R. N. Sen) *J.*, 1910, **97**, 2242; *J.*, 1912, **101**, 1113; (with K. H. Vakil) *J.*, 1918, **113**, 35; (with F. M. Rowe) *J.*, 1918, **113**, 955.

ARTHUR HARDEN

1865—1940

ARTHUR HARDEN died on June 17th, 1940 at his home at Bourne End.

Harden was born in Manchester on October 12th, 1865. His father was Albert Tyas Harden, a Manchester business man, who had married Miss Eliza MacAlister, of Paisley. He was the only son, but there were several sisters, and the family was brought up in an austere nonconformist atmosphere, abjuring the theatre and regarding Christmas as a pagan festival. At the age of seven years he was sent to a private school kept by Dr. Ernest Adam in Victoria Park, Manchester, and four years later he went on to the Tettenhall College in Staffordshire, where he stayed until he was sixteen. In January, 1882, he entered the Owen's College, Manchester, and studied chemistry under Professor Roscoe, then at the height of his fame as a teacher. In 1885 he graduated in the Victoria University with first-class honours in chemistry. A year later he was awarded the Dalton scholarship.

It was J. B. Cohen, to whose stimulating teaching Harden doubtless owed much, who suggested the subject of his first research, "The action of silicon tetrachloride on aromatic amide-compounds", and in the following year the results of this investigation were published in the *Transactions of the Chemical Society* (1886). From Manchester he proceeded to Erlangen, and under the direction of Otto Fischer prepared β-nitroso-naphthylamine and investigated its properties. Having been awarded the degree of Ph.D., he returned to Manchester, and there became first junior and then senior lecturer and demonstrator under Professor H. B. Dixon, who had meantime succeeded Sir Henry Roscoe as Professor of Chemistry. During part of this time Harden shared the laboratory teaching with Hartog (later Sir Philip), and for some years he lectured to the honours students on the history of chemistry, a subject in which he was greatly interested. This interest was shared by Roscoe: together they studied the note-books of Dalton, and arrived at the

[*Photo: Russell.*

[*Reproduced by permission of the Lister Institute of Preventive Medicine.*

ARTHUR HARDEN

conclusion that it was Dalton's investigation of the relations governing the diffusion of gases that led him to formulate his atomic theory. They published their views in 1897 in the *Philosophical Magazine* and in the *Zeitschrift für physikalische Chemie*, and afterwards in a book entitled " A New View of the Genesis of Dalton's Atomic Theory ". Harden's interest in Dalton endured, and in 1915, with H. F. Coward, he communicated to the Manchester Literary and Philosophical Society a description with comments of some of the lecture-sheets with which Dalton used to illustrate his lectures and which had recently been discovered in the rooms of the Society.

In 1895 Roscoe and Harden collaborated in writing a text-book to fulfil the needs of students for the higher South Kensington examination. In collaboration with F. C. Garrett, Harden also wrote a book on " Practical Organic Chemistry ", designed to supplement Perkin's " Organic Chemistry ", and also undertook with Colman the work of revising and editing a new edition of Roscoe and Schorlemmer's " Treatise on Inorganic Chemistry ". All this literary activity served as valuable training for the editorial work which was to occupy so much of the time of his later life.

During these nine years in Manchester Harden seems to have been chiefly interested in his teaching and literary work. He published only two papers based on experimental work; both appeared in the *Transactions of the Manchester Literary and Philosophical Society*, one with W. Haldane Gee on a new form of stereometer (in 1891), and the other on the composition of some iron and bronze implements which had been found by Professor Flinders Petrie in 1897. He began experiments on the combination of carbon monoxide and chlorine, with a view to studying the phenomenon of photo-chemical induction, a subject in which Dixon was especially interested: this work was carried out in collaboration with Dyson, but the results were not published until 1903, six years after Harden had left Manchester. It seems, therefore, that up to the time he left Manchester, at the age of thirty-two, Harden had not manifested an overpowering desire for scientific research. He had applied for the posts of Principal at the Wandsworth Technical Institute and of Inspector under the Science and Arts Department at South Kensington: fortunately both these applications were unsuccessful.

In 1897 Harden was appointed to succeed Joseph Lunt as chemist to the Jenner Institute of Preventive Medicine in London. The choice was made largely on the grounds that he had a wide know-

ledge of chemistry and had proved himself to be a successful teacher. At that time the Institute provided instruction in bacteriology and chemistry for medical practitioners desiring to equip themselves to become Medical Officers of Health. Harden was responsible for the chemical course which was mostly concerned with the analysis of water and foods.

After a few years, however, the London medical schools introduced special teaching for those wishing to qualify for a diploma in public health, so the classes at the Jenner Institute were discontinued, and Harden was henceforth free to devote his whole time to research.

There were then two chemical departments at the Institute (which had meantime changed its name to Lister Institute), one, called Chemical, was under Harden, the other, Biochemical, was presided over by Hedin, with Leathes second in command. In 1905 Hedin left, and Leathes was shortly afterwards invited to occupy a chair of pathological chemistry at Toronto, so the two departments were fused and Harden was placed in charge. In 1912, in recognition of his outstanding work on bacterial chemistry and alcoholic fermentation, he was made Professor of Biochemistry in the University of London.

At the Jenner Institute Harden made his first contacts with biology. His senior colleague was Alan Macfadyen, who was in charge of the bacteriological department, and it was at the latter's suggestion that in 1898 he embarked upon an investigation of the fermentation of sugars by bacteria. The original object of this was to find diagnostic means for the differentiation of varieties of *Bacillus coli*, but Harden gave a wider scope to the research. He kept a carbon balance-sheet by determining the amounts of the various products. Incidentally, he discovered several substances not known at that time to be formed by the bacterial decomposition of sugars. Several products of the fermentation of *B. coli* had been identified earlier, but Harden was the first to construct a picture of the breakdown process as a whole. His first paper on the action of *B. coli communis* and allied organisms on sugars appeared in 1899, and a more extensive account in 1901. In this he compared the results of the fermentation of glucose with that of other hexoses and pentoses and on mannitol and glycerol. He showed that acetic acid and ethyl alcohol were formed in equimolecular proportion and that the two terminal alcohol groups were the source of them. In 1905 he published similar observations upon the action of *B. lactis aerogenes.* With this organism the amounts of acetic acid and

alcohol formed were not equal. One-third of the glucose fermented could not at first be accounted for, and the deficit was found partly in the form of acetylmethylcarbinol and partly in a reduced form as butylene glycol. These two substances had not previously been known to be products of bacterial action on sugars. The former, he found, was the substance responsible for the colour reaction of Voges and Proskauer used as a diagnostic criterion by bacteriologists. Further papers on bacterial chemistry with Norris and with Penfold appeared in 1912.

Harden's work on bacterial chemistry did not attract as much attention at the time as its merit justified. The bacteriologists did not appreciate what it was about, and it was too far removed from the interests of all but a few chemists. It was, indeed, pioneer work, and formed the basis on which many interesting researches into bacterial metabolism have subsequently been built.

Harden commenced to work on bacterial chemistry in 1897, and in 1900 he started his researches on alcoholic fermentation, in the course of which he made some notable discoveries which will remain associated with his name. These two lines of research proceeded simultaneously for some ten years, but for simplicity of description they are dealt with separately.

Alcoholic Fermentation.

Harden derived his interest in alcoholic fermentation also from his bacteriological colleague, Alan Macfadyen, who, like most microbiologists, was impressed with Buchner's discovery that the cell-free juice expressed from yeast would ferment sugar.

The belief that alcoholic fermentation required the operation of the intact living cell having been superseded, a new experimental method for its study had been found. The first crude preparations of zymase had, however, two drawbacks: (1) yeast juice produced a considerable amount of alcohol and CO_2 without the addition of sugar; (2) it rapidly lost its power to ferment. Harden's first researches were concerned with discovering the cause of these disturbing phenomena with a view to overcoming their hindrance to quantitative experimentation. Autofermentation he found to be due to the action of the enzyme upon the glycogen expressed from the yeast cells and that it ceased when this supply was exhausted. Deterioration in fermentative activity, he concluded, was brought about by destruction of the zymase by the proteolytic enzyme also present

in the expressed juice, for by the time autolysis was advanced its power to ferment had disappeared.

It was whilst engaged on these investigations, neither of which had direct significance for the understanding of the chemistry of the transformation of sugar into alcohol and CO_2, that he made two fundamental discoveries. The first was that the enzyme zymase would not convert sugar into alcohol unless another substance which functioned as a co-ferment was present. The second was that the presence of phosphate was also necessary.

It is doubtful whether Harden would have made the advances he did had he not early abandoned the gravimetric measurement of CO_2 produced, which had been used by Buchner and others, and adopted a volumetric one. The simple method he substituted enabled him to make frequent determinations of the CO_2 evolved and thereby study the progress of the reaction at ten-minute intervals, if necessary, throughout the period of the experiment.

In his studies on alcoholic fermentation Harden was powerfully supported by the able pupils and collaborators whom he had attracted to his laboratory. Notable amongst these were W. J. Young, who became Professor of Biochemistry in the University of Melbourne; R. Robison, who succeeded him; Lord Henley; and Miss Macfarlane, who carried on the good work at the Lister Institute. These collaborations with younger folk were happy and fertile. Harden's strong points as an investigator were his wide knowledge of chemistry and his capacity to analyse the results of an experiment dispassionately and define accurately what interpretations were justifiable. He was a superb critic but unduly suspicious of adventures into the realm of imagination.

The Co-enzyme.

How Harden came to discover co-zymase and the rôle of phosphates in alcoholic fermentation makes an interesting story which indicates his measure as an investigator.

For some reason or another, which is not now material, he added boiled autolysed yeast juice to a mixture of zymase and sugar solution and found that the rate of fermentation was thereby greatly increased. At first he attributed this to some restraining influence on the proteolytic enzyme, always present with zymase, which he had previously found to be inhibited by horse serum and other proteins. This explanation had, however, to be put aside after appropriate experiments, and he was faced with the fact that yeast

juice contained, in addition to zymase and a proteolytic enzyme, a substance stable to boiling which favourably influenced fermentation. Additional study of its properties showed that it was thermostable, dialysable through parchment paper, destroyed by incineration, and precipitated by 75 per cent. alcohol.

Further than this he could not advance until some satisfactory method of separating the unknown substance from zymase was found. Dialysis was too slow, for meantime the zymase was being destroyed by the proteolytic enzyme.

The separation was ultimately achieved by employing a Martin gelatin filter, by means of which a separation could be effected in a few hours, the zymase remaining on the outside of the filter and the activating substance passing into the filtrate. Neither the redissolved residue nor the filtrate alone would ferment, but when the two were mixed fermentation occurred at about the original rate. For this necessary adjunct to fermentation by zymase the name co-ferment was suggested.

Harden did not discover more as to its nature beyond finding that it contained phosphoric acid in its make-up, nor as to what stage in the conversion of sugar to alcohol it was operative, but he did hazard the suggestion that as it contained phosphate it might be involved in the phosphorylation of the hexose, which he had also discovered to be an essential stage in the process and which will be dealt with immediately. The constitution of the co-ferment was ascertained by von Euler some years afterwards. He showed that it was a complex nucleotide containing adenine, nicotinic acid, and ribose, and proposed the name co-zymase for it.

The Essential Rôle of Phosphates.

Experiments with boiled yeast juice also led Harden to discover the necessity for phosphates in fermentation by zymase. As just mentioned, the co-ferment was destroyed by incineration, and could be precipitated by 75 per cent. alcohol, but the ash or the filtrate after precipitation still produced a temporary increase in the production of CO_2.

This result led to the trial of the addition of potassium phosphate. The result was startling. In fifteen minutes the rate of production of CO_2 had increased sevenfold. It then fell as rapidly to the original rate. It was much as if an acid had been added to a solution of bicarbonate, for the amount of CO_2 produced was equimolecular with the phospate added.

This and the fact that it could be repeated indicated that the phosphate had somehow become fixed. This was proved by showing that the phosphate was no longer precipitable by magnesia mixture. Harden and Young subsequently found that it had combined with the sugar to form a hexosediphosphate. This ester was subsequently isolated and identified by Young.

The study of the fermentation of mannose and fructose threw further light on the constitution of the hexosephosphate. Fructose was fermented more rapidly than mannose or glucose. The rate of fermentation of all three sugars was accelerated by phosphate, but that of fructose was double that of glucose or mannose and it was much less rapidly inhibited by the further addition of phosphate. The hexosediphosphate prepared from these three sugars was identical and the quantitative relations were expressed by the same equations. It was suggested that the hexosephosphate was probably derived from the enolic form common to the three sugars, though the possibility that the two molecules of sugar were broken down into smaller groups and hexaphosphate resynthesised from these was considered possible.

As fermentation by the intact yeast cell proceeds at a uniform and enhanced rate compared with that by zymase, it was clear that the bound phosphate must be liberated as quickly as it was formed. Harden and Young soon discovered that yeast contained a phosphatase which hydrolysed hexosediphosphate, so presumably this accounted for its non-accumulation, and they thought that this mechanism must be defective in the case of yeast juice and so account for the relatively slow rate of fermentation.

Experiments were therefore made in which phosphatase prepared from yeast was added to a zymase preparation in which fermentation had nearly ceased after the spurt occasioned by addition of phosphate. The addition of phosphatase caused the fermentation rate to increase much as if a new dose of phosphate had been added, but it could not be maintained, although the increased rate endured longer than when phosphate was added. The conditions obtaining in the living cell could not be completely imitated in zymase fermentation, as for some reason the added phosphatase lost its activity, but it could be done indirectly by the addition of arsenates—a result no one could have foreseen. As Harden said in his Nobel lecture, " this observation was the undeserved reward for thinking chemically about a biochemical problem, a dangerous thing to do ". As in many chemical reactions arsenates behave like phosphates,

out of curiosity he tried whether they could replace them in alcoholic fermentation. He found they could not. The addition did indeed increase the rate of fermentation, but the effect was not sudden and temporary as that of phosphate, but slower and more lasting. Arsenates behaved in an entirely different way, apparently by preventing the destruction of phosphatase.

Harden and Young suggested that their observations indicated that fermentation could be illustrated by two equations :

$$(1)\ 2C_6H_{12}O_6 + 2Na_2HPO_4 = C_6H_{10}O_4(PO_4Na_2)_2 + 2H_2O + 2CO_2 + 2C_2H_6O;$$

$$(2)\ C_6H_{10}O_4(PO_4Na_2)_2 + 2H_2O = C_6H_{12}O_6 + 2Na_2HPO_4$$

the first representing the evolution of CO_2, production of alcohol, and accumulation of phosphoric ester, the second the hydrolysis of the ester with liberation of a hexose and mineral phosphate.

In the presence of arsenate, equation (2) proceeds sufficiently rapidly to supply phosphate so that equation (1) proceeds with maximal velocity.

In 1914 Harden and Robison discovered that the diphosphate was not the only phosphate ester formed during fermentation, but that hexosemonophosphate was also present. The relative amount of these two phosphates varied from 80 per cent. of one or the other according to circumstances. Nevertheless the ratio of CO_2 evolved to PO_4 esterified remained constant and approximately unity. What were the conditions for the preferential formation of the mono- or di-phosphate could not be discovered. Harden was convinced that complete reaction of some sort took place as the result of which two phosphate groups were introduced into certain sugar molecules—either into the same molecule or one each into two different molecules—and this induced the decomposition of another molecule of the carbohydrate. Robison and he showed that the monophosphate reacted with a further quantity of phosphate and was accompanied by an increased production of CO_2.

Harden recognised that the only quantitative relation that his experiments had established was that during the course of fermentation by yeast juice, or by dried yeast, for every one molecule of phosphate esterified approximately one molecule of CO_2 was evolved.

This view and its expression in the form of the equations (1) and (2) above truthfully expressed the beginning and the end of the reactions and the final result. The intermediate stages, however, still remained obscure, and it was not until Meyerhof and his colleagues

showed that the monophosphate was the first product, and that hexosediphosphate was formed by the further phosphorylation of the monophosphate, which was then converted into two molecules of triosephosphate, that the course of the breakdown began to be clearer.

Henceforth, with the exception of the war years, 1914–18, most of Harden's research activities were devoted to attempts to elucidate the reactions involved in fermentation and the rôles played by zymase, co-zymase, and phosphates respectively. It was a period of controversy, with experiment and counter-experiment, and it is difficult to make a connected story of Harden's contributions, for the significance of individual experiments is not easily apparent.

Buchner's suggestion that lactic acid was an intermediate in sugar fermentation was rejected by Harden, a view in which Buchner eventually concurred, though unfortunately not before it had been widely accepted by biologists. Iwanoff claimed to have isolated a triosephosphate giving an osazone (m. p. 128°) similar to one prepared by Lebedeff from the oxidation products of glycerol. According to Iwanoff the formation of hexosephosphate preceded the alcoholic fermentation and the amount of fermentation should be found proportional to the amount of hexosephosphate decomposed. Harden did not at first accept this view, but the existence of Iwanoff's triosephosphoric acid was confirmed in 1907 by his colleague Young, who isolated it as a lead salt. No attempt seems, however, to have been made by Harden to introduce the triosephosphate into his equations. It was shown by Macfarlane, working in Harden's laboratory, that an autolysed solution of dried yeast which was incapable of fermenting glucose even after the addition of the co-enzyme could decompose hexosediphosphate, producing inorganic phosphate and CO_2. The existence of a definite phosphatase acting on the hexosediphosphate was therefore established. When co-enzyme and arsenate were added the decomposition of the hexosediphosphate was extremely rapid, and CO_2 and inorganic phosphate appeared as final products of the decomposition. It was the breakdown of the hexosediphosphate that was stimulated by the presence of arsenate.

Eighty per cent. of the great fall in fermentative activity which occurred when fresh yeast was converted into yeast juice was found to occur during the process of grinding, and it was during the same period that the yeast acquired the power of responding to phosphates. It was therefore concluded that the phosphatase was destroyed.

The nature of the enzymes in yeast and their methods was investigated by Harden and his colleagues in a long series of researches. He confirmed Neuberg's discovery of the existence of the enzyme carboxylase in dried yeast, which split pyruvic acid into CO_2 and acetaldehyde, and showed that, as this reaction took place after the co-enzyme had been completely washed away, it was independent of the presence of the co-enzyme. The reducing power of zymin or dried yeast, on the other hand, was removed by washing, but could be restored by the addition of the boiled washings. Certain aldehydes also restored the reducing power and therefore had the property of acting as oxygen acceptors. Similar experiments carried out with washed rabbit's muscle showed that here the addition of either lactic acid or acetaldehyde restored the reducing power. Evidence was also obtained of the existence of a peroxidase in fresh yeast. The peroxidase activity was lost on drying for seventeen hours at 37° C., but was again detected after the dried yeast had been washed. The catalase activity was not affected by washing, whereas invertase, but not maltase, was removed by washing the dried yeast. Harden also showed that the presence of inorganic salts exercised a marked influence on the autofermentation of yeast; all dissolved substances which plasmolysed the yeast cell caused also a large increase in the rate of autofermentation. Washed zymin in the presence of a suitable concentration of sodium phosphate was activated by potassium pyruvate, but not by acetaldehyde; if, however, the sodium phosphate were replaced by the potassium or ammonium salt, acetaldehyde also acted as an activator. There was therefore a specific salt effect, the sodium ion acting differently from the potassium or ammonium ion. On the other hand, when the fermentation of fructose or glucose by dried yeast preparations was examined it was found to be equally depressed by the addition of sodium or potassium chloride and the effect of the sulphates was somewhat greater. This action was shown to affect the rate of action of the hexaphosphatase, but not that of the carboxylase. Potassium phosphate was also shown to produce a depressing effect, but in this case, unlike that of the sulphate, the depressing effect could be largely counteracted by the addition of acetaldehyde to the solution.

Application of Harden's Discoveries to Bacterial Metabolism and Animal Physiology.

After Harden's discovery of the co-enzyme and of the important part played by phosphates and phosphoric esters in alcoholic

fermentation, it was soon discovered by various workers that phosphorylation provided the clue to many other biological phenomena.

Harden's earlier work on bacterial metabolism was done before his studies of fermentation by yeast had revealed the importance of phosphorylation as a factor in the latter. He did not himself undertake experiments to decide whether it would prove of equal importance in the former. During recent years, however, the work of many investigators has shown that this is actually the case. During glycolysis under the influence of *Bacillus coli*, for instance—the bacterium which had been Harden's chief concern—the main stages of breakdown are undergone by phosphorylated molecules. In brief, the following sequence occurs: Hexosediphosphate yields phosphoglyceraldehyde. By dismutation this yields 1-glycerolphosphate and phosphoglyceric acid. Of these two products the former breaks down into ethyl alcohol and free phosphates, while the latter yields phosphopyruvic acid. In aerobic conditions this last product breaks down into free phosphate, acetic acid, and CO_2; while anaerobically formic acid takes the place of CO_2. The liberated inorganic phosphoric acid becomes available for the further formation of the original hexosephosphate.

An astonishing degree of similarity was also found to exist between almost every detail of the production of lactic acid by the muscle enzymes and of alcohol by the yeast enzymes, which extended to the identity of the phosphoric esters concerned, the accumulation of ester under similar conditions, and even to the effect of arsenates on the process.

In an aqueous extract of muscle glycolysis proceeds, but neither glycogen nor glucose molecules suffer change until they have become associated with phosphoric acid as its esters. The various simpler molecules which represent intermediate stages in the sequence of anaerobic reactions which ultimately liberate the available energy of the original carbohydrate molecules also undergo esterification or suffer substitution by the phosphoryl radical. Of fundamental importance in maintaining the sequence of events is the circumstance that the phosphoryl radical is readily transferable from one molecule to another, from a donator of phosphate to a receptor. Such transference leads to the coupling of reactions, and in particular cases may result in the actual transference of energy from exothermic to endothermic events. The study of these phenomena gained much in interest when it was shown (in the school of Parnas in Lwow; in Cambridge

by D. M. Needham and van Heyningen, and by Meyerhof and collaborators) that the progress of the reactions depends in general on the presence of adenylic acid in muscle. It has been shown, for instance, that the events which yield the lactic acid of anaerobic glycolysis involve an oxido-reduction reaction strongly exothermic in character. It comprises an oxidation of glyceric aldehyde and a simultaneous reduction of pyruvic acid. In the absence of either inorganic phosphate or adenylic acid, however, this reaction does not occur. In their presence it actively proceeds, yielding the energy for a strongly endothermic reaction, namely, the esterification of adenylic acid to adenose pyrophosphate. This latter is a compound with high free energy content, exerting indispensable functions both as a donator and as a receptor of the phosphoryl ion. On hydrolysis its energy is liberated, and it is indeed legitimate to speak of the energy of phosphate bonds. It would seem that the myosin of the muscle fibres itself catalyses the dephosphorylation of this pyrophosphate. It is likely, therefore, that a local breakdown in the fibres yields, or contributes to, the energy necessary for muscular contraction. The pyrophosphate structure is then reconstituted by transference of phosphoryl from yet another muscle constituent, namely creatin phosphate, which may be looked upon as a phosphate accumulator.

It is of interest to find that another aspect of Harden's work, namely, his demonstration of the effect of arsenate, has greatly assisted towards an understanding of the mechanism of the reactions just described. At the same time, the muscle studies have more fully explained the effect of arsenic on alcoholic fermentation.

This brief account omits many details now known concerning the events in muscle, nothing, for instance, being said about the enzymes which catalyse the reactions. It should make clear, however, the remarkable lines on which the influence of phosphates is exerted. Recognition of the significance of Harden's discoveries constituted a turning point in the history of muscle chemistry.

Robison's significant observations on ossification were also a direct outcome of his association with Harden in work on fermentation. The question why calcium and phosphorus should be normally deposited in cartilage that was about to ossify and only pathologically elsewhere remained unanswered. It occurred to Robison that there must exist in ossifying cartilage some conditions producing supersaturation of calcium and phosphate ions, and that one way in which this might occur would be by the decomposition locally of phosphoric esters in the blood supplied, supposing the

tissue contained phosphatase. On examination it was found that cartilage about to ossify did indeed contain a phosphatase, whereas it was absent from the cartilages of the patella and of the trachea which did not undergo ossification.

When war broke out in 1914, the Lister Institute soon became depleted of most of its male staff and research students, while those who remained concerned themselves with problems having some relationship to our state of belligerency. Harden was left in charge of the Institute during the absence of the director on military service. Wanting to devote himself to some subject which would contribute to the war effort, he abandoned his researches on alcoholic fermentation for five years and investigated two of the then known accessory food factors or vitamins, lack of which there was good reason to believe was responsible for the diseases beri-beri and scurvy respectively. Both of these diseases had occurred amongst our troops at outposts in Asia and Africa, where, either from difficulty of transport or from being beleaguered, they had to subsist on a restricted diet. The study of accessory food factors had assumed military importance and the exploration of means of effectively supplementing rations had become a matter of some urgency. These investigations were not confined to the application of existing knowledge, but involved work of a fundamental character, as nothing was known of the chemical composition of the two factors and little about their properties. In carrying them out, Harden had valuable assistance from S. S. Zilva, then a research student in his department.

They proved that neither 2-hydroxypyridine nor adenine was the active agent which cured beri-beri, as had been stated. The two water-soluble factors were differentiated by the use of fuller's earth, which absorbed the antineuritic but not the antiscorbutic factor. The former was shown to be essential for the growth of frogs. The fruit-fly *Drosophila* was found to need the antineuritic but not the antiscorbutic. The biological synthesis of the antineuritic by yeast was established.

Holst's experiments showing that scurvy was a dietary disease due to a deficiency of a specific substance were confirmed, and a step towards the separation of this principle was achieved by removal of the organic acids, carbohydrates, and protein from lemon juice and the production of a residue of much increased potency. In collaboration with Dr. Still, the superiority of this concentrated product in the treatment of infantile scurvy was demonstrated.

The susceptibility of the antiscorbutic principle to adverse

influences was studied and its particular sensitivity to alkalis discovered. The effect of heating and storage at different temperatures on the potency of fruit juices was investigated and results of immediate practical importance obtained.

Scurvy was produced in monkeys by a scorbutic diet and the relative antiscorbutic requirements of this animal ascertained. Rats, on the other hand, did not develop scurvy.

As, in older days, fresh ale had a reputation for antiscorbutic properties, and yeast being one of the richest sources of the antineuritic principle, stout, ale, and fined beer were tested, but both principles were found lacking in all of them.

Although research on nutrition had not been Harden's *métier*, he adapted himself to work in this new field with conspicuous success, and the results achieved make a goodly contribution to the early development of our knowledge of accessory food factors. Incidentally, it led to his acquiring a wide knowledge of the subject, which was used to good effect in editing the three editions of "Present Knowledge of Accessory Food Factors", published by the Medical Research Council in 1919, 1924, and 1932.

Recognition of the importance of Harden's researches came from many quarters. In 1909 he was elected a Fellow of the Royal Society, and in 1935 was awarded the Davy Medal by the Society. He served on its council from 1921 to 1923. In 1929 he shared the Nobel prize for chemistry with von Euler. The Universities of Manchester, Liverpool, and Athens conferred honorary degrees upon him, and the Kaiserlich Leopold Deutsche Akademie der Naturforscher of Halle elected him to its membership. In 1936 he received the honour of knighthood.

An account of Harden's scientific career would be incomplete without some reference to his teaching ability and his literary activities. In the early days at Manchester his powers as a teacher were recognised. At the Lister Institute he had little opportunity to exercise this gift in which he found pleasure, but for many years he devoted one evening a week to a class in microbiology at the Sir John Cass Institute, and for a while gave a course of evening lectures on biochemistry at the Chelsea Polytechnic. In both he took the greatest pains and interest.

Literary work took up a good deal of his time. Beside the very onerous work of editing the *Biochemical Journal*, he wrote the article on "Fermentation" for Thorpe's "Dictionary of Chemistry" and the section on yeast enzymes for Oppenheimer-Pincussen's "Die

Fermente und ihre Wirkungen" and the section on alcoholic fermentation, "The Early Stages of Fermentation in the Yeast Cell", for "Die Ergebnisse der Enzyme Forschung", and he was the author of the monograph on Alcoholic Fermentation in the Longmans series of "Biochemical Monographs."

Harden's outstanding qualities as an investigator were clarity of mind, precision of observation, and a capacity to analyse dispassionately the results of an experiment and define their significance. He mistrusted the use of his imagination beyond a few paces in advance of the facts. Had he exercised less restraint, he might have gone farther; as it was, he had little to withdraw.

His personal relations with his fellow-men were controlled by an uncommon reserve. His attitude to most was that of a benevolent neutral. Few reached intimacy with him, but those who did penetrate his protective covering found in him a lovable and staunch friend.

He was generally cheerful, but never exuberant and suspicious of exuberance in others. He had a dry humour and was capable of unexpected flashes of wit. It was not his habit to offer his opinions unasked, but his advice and help were freely given if called for.

He had a very equable temperament, and said that he had never known great elation or great depression. The uncommon control he exercised over his emotions was perhaps attributable in part to the severe puritanical discipline of his early life. Whatever the cause, his judgment was little influenced by them, so that he was pre-eminently a fair man. He would have made a great judge.

In 1890 he married Georgina Bridge, of Christchurch, New Zealand. His wife died in 1928; they had no children.

In 1930 he retired from his professorship at the Lister Institute, but continued to come every day to his laboratory, carrying on experimental work and correcting proofs for the *Biochemical Journal* until a year or two before his death. Towards the end of his life he suffered from a progressive nervous disease from which release came before it had become too irksome and while he still enjoyed his garden, his books, and his interest in science.

W. J. Pope

WILLIAM JACKSON POPE

1870—1939

William Jackson Pope, the eldest of eight children, was born at 89 New North Road, London, on March 31st, 1870. His father, William Pope, was a native of Biggleswade who came to London in 1858, and in 1869 married Alice Hall of Prudhoe, Northumberland. Both parents were staunch and active members of the Wesleyan Methodist Connection and regular attendants at Wesley's Chapel, City Road, of which William Pope was a Trustee for many years. He served also as one of the managers of the Radnor Street Schools attached to the City Road Circuit, and exercised considerable influence in directing its affairs. Serious, though without the least austerity, the early home training was undoubtedly a contribution towards the characteristic thoroughness which distinguished Pope in all his scientific work.

In January, 1878 Pope entered the Central Foundation School, where he received a thorough grounding in subjects of great value to him in later life. His ability to learn quickly gave him leisure to pursue particuliar interests, and at the age of twelve he had in his bedroom cupboard a collection of chemicals and simple apparatus with which he made experiments, delightful to the younger members of the family but not always viewed with favour by his seniors either at home or at school. One of the earliest *X*-ray photographs taken in London was of his hands. This showed clearly a mis-shaped bone due to an unexpected explosion which terminated one of these experiments.

Whilst at school Pope acquired great skill in the practice of photography. At that time the operator had to conduct all the processes of developing and printing, and the fact that a large number of his photographs more than fifty years old are still in perfect condition affords direct evidence of his complete dexterity in his youth. In later years he had less time to devote to the practical side of the work, though he followed with great interest the development of both aerial and colour photography.

Pope had a natural aptitude for acquiring foreign languages, in which capacity he was of assistance to his father, who was interested in the manufacture of bricks in Belgium and their export to this country. He became proficient in both French and German whilst still in his teens, and at the age of fifteen was using a book of German mathematical tables, which was lying on his study desk at the time of his death. His fluent French and German proved invaluable in later years and singled him out to represent this country with significant success at international conferences called for the discussion of chemical theories and industries.

He took no part in sport, a circumstance probably attributable to an eyesight defective from childhood, but he was a prodigious walker and particularly interested in matters relating to dogs and birds. He was a capable violinist and for many years played in an amateur orchestra. In later life his work afforded him little leisure for this recreation.

He left school in August, 1885, having obtained full marks at the midsummer examination in both Theoretical and Practical Chemistry and being recorded as specially distinguished in " Theory of Music ". He was given an entrance scholarship at the Finsbury Technical College, where he worked till 1887, when he was awarded a Mitchell Scholarship tenable at the City and Guilds College, South Kensington. Here he at once attracted the attention of Armstrong, who, on Pope's receiving the Associateship of the College, made him a member of his staff. In 1897 he was appointed as chief of the Chemistry Department of the Goldsmiths' Company's Institute at New Cross and was thus brought into contact with the Clerk of the Company, Mr. W. T. (later Sir Walter) Prideaux. The Goldsmiths' Company over a long period of years has shown its practical interest in the advancement of Chemistry. In this connection it may be remembered that when in 1886 Longstaff offered £1000 to the Chemical Society towards the establishment of a Research Fund provided others would make up a like amount, the Court of the Company forthwith contributed the whole sum required. Pope's work at the Institute and his long association with the City and Guilds Colleges, which owe so much to the munificence and fostering care of the Goldsmiths, led ultimately to his being given the Freedom and Livery of the Company by special grant in 1919. Two years later he was elected a member of the Court and in 1928—29 served as Prime Warden. His collaboration then became most valuable in assuring that the large sums voted by the Company for technical

education should be applied to the fullest advantage. Pope interested himself in all questions relating to gold and silver plate and to the Hall Marking laws. He presided at many meetings organised by the Company to consider matters affecting the manufacture of silver. At these discussions his wide knowledge of the industry and his unfailing tact helped greatly in securing agreement and in solving the difficulties which arose from time to time. In 1922 the Company appointed him one of their representatives on the Council and the Executive Committee of the City and Guilds Institute. Ten years later he accepted the Chairmanship of the Council, a position he occupied with great distinction till his death.

Pope was appointed head of the Chemistry Department of the Municipal School of Technology and Professor of Chemistry at Manchester in 1901 and seven years later was elected to the Chair of Chemistry at Cambridge in succession to the veteran Liveing. His voluminous scientific work is outlined elsewhere, but it is noteworthy that he had the none too common gift of being able to apply his knowledge in the interests of the community. This was recognised during the First World War when he became a member of the panel of consultants of Lord Fisher's Board of Invention and Research. He devoted himself wholeheartedly and with consummate skill to those chemical problems arising from the war, towards the solution of which his vast knowledge, acquired by wide reading, proved of the utmost value, particularly in connection with the sources of materials needed for high explosives. Later, when the Germans used poison gas, he developed the ethylene process for the direct synthesis of mustard gas. At the end of the war these services were recognised by his receiving a Knighthood of the Order of the British Empire.

As a lecturer he had the flair which combines easy delivery with clear statements and invariably attracted the closest attention of his audience. In the laboratory his methods developed initiative, to which he gave full encouragement and active support whilst interfering with the worker as little as possible. In this way he succeeded not only in winning the confidence of his staff and students but also in obtaining the best results from their work. But Pope was other than a mere academic professor, for he possessed marked power of organisation. In his address from the Presidential Chair of the Chemical Society in 1918 he directed attention to the urgency of bringing into line the societies representing pure and applied chemistry, and later was largely instrumental in forming the

Federal Council for Pure and Applied Chemistry, of which he served as the first Chairman. In collaboration with leading chemists on the Continent he created the *Union Internationale de Chimie* having the like object of co-ordinating the work of societies of different nationalities. He was President of this federation in 1923, when many distinguished British and foreign chemists attended the Fourth International Chemical Conference, held in Cambridge. He also presided during a long period of years at the Chemical Conferences of the Solvay Foundation in Brussels. His services to this Foundation were recognised in 1937 when he was created a *Grand Officier de l'Ordre de Léopold*. He was awarded many medals, including the Davy Medal of the Royal Society, numerous Honorary Degrees of Universities and the Membership of leading English and foreign Scientific Societies. With all these high distinctions he referred to none with greater pleasure than to the first medal he received whilst still a boy and a student at Finsbury, a bronze medal for distinction in Coal Tar Products awarded at the examinations of the City and Guilds of London Institute.

In his later years Pope would often refer to himself as a machine, a most unsuitable description of a man characterised by his broad outlook. Always willing to afford help to friends and colleagues in any matter in which he could assist, many of those with whom he associated made serious claims on his time. He systematically overworked himself and was left little opportunity for leisurely enjoyment of hobbies. None the less he was able at times to attend sales at Christie's and elsewhere and thus to add to his almost unique collection of chemical paintings and engravings and of medieval pharmaceutical jars and mortars. Pope's interests were unusually wide. He was equally at home at the Garrick Club with his theatrical friends as when he was presiding over an international gathering of eminent chemists. He was invariably full of humour, which was whetted by his critical faculty. No more amusing example of this can be cited than his letter to *The Times* on American safety razor blades. The works manager of a Sheffield firm had given evidence before the Standing Committee of the Board of Trade on imported cutlery, in which he had stated that the total annual import of one type of American safety razor blade if spread out would cover England eight times over. This was widely reported in and accepted by the Press without comment, until Pope's letter, appearing a few days later, in innocently worded terms pointed out *inter alia* that if the contention of the witness was taken seriously, as no doubt it

should be, it disclosed who paid the supertax, since each inhabitant of the country must be spending more than £150,000 per annum on safety razor blades.

Pope was a bachelor. As a genial and considerate host he will be best remembered by his friends. In his own home and amongst intimates the air of concentration often mistaken for gloom was absent and he showed himself human and entertaining. He was a raconteur of delightful stories, which might have emanated from some eminent actor or ambassador rather than from a learned chemist. Modest in mien and an authority in every branch of his own subject, Pope showed remarkable versatility. This made him a delightful companion even amongst those who had no training in chemistry, whilst his fellow chemists often failed to recognise that he was well versed in questions relating to literature and to art. The passing of his engaging personality leaves a void amongst his friends which cannot be filled. No longer will they be able to enjoy association with one of whom it may truly be said, he passed through life

> " Wearing all that weight
> Of learning lightly like a flower."

The Scientific Work of William Jackson Pope.

Pope began his scientific career at the Central Technical College (then the City and Guilds of London Central Institution) in a most stimulating environment. Armstrong was at the height of his powers. His well-known views on aromatic substitution and on the origin of colour had recently been put forward and investigations on these subjects were being actively pursued in his laboratory. But though this work was claiming most of his attention, he still maintained his interest in the chemistry of camphor and the terpenes and Pope's first scientific publication was a joint paper with him on an investigation in this field.

It had been generally supposed that turpentines from different sources differed because they contained different terpenes. Armstrong, however, thought that they contained different proportions of the antimeric forms of the same terpene. Since the terebenthene (pinene) from French oil of turpentine showed a uniform high lævorotation and that from the American oil a smaller and variable dextrorotation, Armstrong suspected that the French oil was practically pure *l*-pinene and the American a mixture of *d*- and

l-pinene with the former in greater or less excess. He was strengthened in this belief by finding that an oil of turpentine from the Burmese *Pinus Khasyana* (received from Kew) was apparently the optical counterpart of the French oil.

Seeking some characteristic crystalline derivative through which pinene could be identified, he thought of utilising the old observation of Sobrero (1851) that the terpene fraction of oil of turpentine yielded a solid compound, $C_{10}H_{18}O_2$, on prolonged exposure to moist oxygen in sunlight. For this compound Armstrong proposed the name *sobrerol* and he and Pope studied the production of sobrerol from turpentines of different origin (*J.*, 1891, **59**, 315).

They showed that sobrerol was an optically active compound and that the optical antimers crystallised in enantiomorphous hemihedral forms and combined to give a racemic modification. French turpentine yielded nearly pure *l*-sobrerol and Burmese pure *d*-sobrerol. The American oil, however, gave mixtures partially separable by crystallisation, the earlier fractions being pure *d*-sobrerol, the later containing increasing proportions of *l*-sobrerol. Armstrong's views on the nature of the terpenes in these turpentines were thus confirmed.

The value of the paper depended largely on the crystallographic observations and for these Pope was responsible. In an explanatory paper (*ibid.*, p. 311) preceding the joint publication Armstrong made the acknowledgement that the possibility of " collating the scattered results of earlier work " had been " chiefly owing to the important assistance which one of my students, Mr. Pope, has rendered me in submitting the products to crystallographic examination ".

About the time that this work was finished Marsh and Cousins published an account of the preparation of sulphonic derivatives of chloro- and bromo-camphor by means of chlorosulphonic acid (*J.*, 1891, **59**, 966). As Armstrong had long been interested in the action of sulphuric acid on camphor—he had worked on this subject with A. K. Miller many years previously (*Ber.*, 1883, **16**, 2255)—he asked Pope to repeat Marsh and Cousins's work.

Pope's first attempts were not very successful. They resulted in a tar-like product which he took in a porcelain basin to his colleague, F. S. Kipping, then newly arrived from the Heriot-Watt College, Edinburgh, where he had been with W. H. Perkin. This was the beginning of a collaboration which lasted for several years and had an important effect in determining the subsequent direction of Pope's work.

It was known that camphor could not be sulphonated by ordinary concentrated sulphuric acid, for this converts it into " camphren ",

shown by Armstrong and Kipping to be a mixture, chiefly of carvenone and 3 : 4-dimethylacetophenone (*J.*, 1893, 63, 75). Kipping and Pope found, however, that it was sulphonated by fuming sulphuric acid and also, as had been found by Marsh and Cousins for the halogenocamphors, by chlorosulphonic acid. They soon discovered that the sulphochlorides, described by Marsh and Cousins as non-crystallisable, were in fact when pure substances of exceptional crystallising power. The same was true of many of their derivatives (*J.*, 1893, 63, 548; 1895, 67, 354).

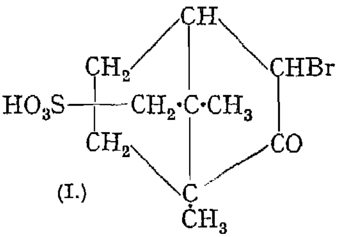
Pope was thus afforded abundant opportunity to develop his great talent as a crystallographer. Most of his earlier work was strongly influenced by his interest in crystallography, and Professor F. S. Kipping says, " I think that the happiest hours of his life were those spent in the dark room with his goniometer, in calculating the results of his measurements and in drawing the crystal figures. He seemed never to tire of this work and his desire for new compounds to measure was almost insatiable."

Kipping and Pope further discovered that the camphorsulphochlorides and bromides, when heated, decomposed smoothly with the elimination of sulphur dioxide, forming halogenocamphors. These derivatives were different from those formed by the direct halogenation of camphor and were named " from their pyrogenic formation " π-derivatives (*J.*, 1895, 67, 371).

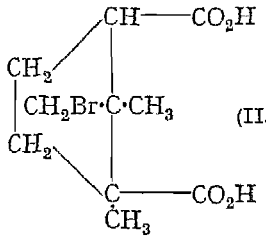
By degradation of bromocamphorsulphonic acid Kipping was able to effect transformations which evidently involved the following structural changes :

$$-CH_2 \cdot SO_3H \longrightarrow -CH_2Br \longrightarrow -CO_2H$$

Sulphonation had therefore taken place in a methyl group, and, since the carboxyl finally produced was on a different carbon atom from either carboxyl of camphoric acid, the methyl group sulphonated was one of those of the *gem*-dimethyl group. On the basis of the Bredt camphor formula α-bromo-π-camphorsulphonic acid therefore had the structure (I).



(I.)



(II.)

Oxidation of $\alpha\pi$-dibromocamphor gave π-bromocamphoric acid (II), which, treated with alkali, yielded a *trans*-lactone. The π-position is therefore in the methyl group of the *gem*-dimethyl pair remote from the carbonyl group (*J.*, 1896, **69**, 913).

By these discoveries the preparation of many new halogeno-derivatives of camphor became possible and seven such compounds were prepared and characterised. The study of these substances, besides revealing crystallographic relationships, led to various observations of theoretical interest. Thus, *d*-camphor when sulphonated underwent racemisation, yielding a mixture of *d*- and *l*-camphorsulphonic acids. Kipping and Pope pointed out the surprising character of this observation (*J.*, 1897, **71**, 956). Profound intramolecular changes would be needed for the inversion of a tricyclic compound of the Bredt formula. Kipping and Pope considered that the racemisation showed "that part of one closed carbon chain may be caused to rotate about another", but it is difficult to believe that a change of this kind could be brought about by thermal processes at 100° and one is tempted to look for some chemical mechanism. Armstrong and Lowry, who subsequently discussed the question (*J.*, 1902, **81**, 1469), regarded the racemisation as a result of rupture and re-formation of the bond between the $C(CH_3)_2$ and the $CH{\cdot}CH_3$ group.

Another result of these investigations was the discovery of *pseudo-racemism* (*J.*, 1897, **71**, 989). This resulted from the crystallographic comparison of the optically active and inactive forms of two compounds obtained by the degradation of bromocamphorsulphonic acid, *trans*-camphotricarboxylic anhydride and *trans*-π-camphanic acid hydrate. The inactive forms of these substances were found to resemble their active components in crystalline characters so closely as to make their crystallographic distinction difficult. The same phenomenon was shown by camphorsulphonyl chloride. Since the racemic and the optically active modifications of a substance must differ markedly in crystal structure, the inactive compounds could scarcely be normal racemates. Further investigation showed that they were conglomerates of a peculiar type formed of alternate twined layers of the enantiomorphs. For non-homogeneous crystalline associations of enantiomorphs of this kind Kipping and Pope proposed the name *pseudo-racemate*. The sense in which pseudo-racemism was understood by the originators of the word is thus very different from that in which it was subsequently employed by Roozeboom, who used the term to denote a homogeneous solid solution of enantiomorphs.

An investigation which combined Pope's two chief interests—stereochemistry and crystallography—was concerned with the crystallisation of sodium chlorate (*J.*, 1898, **73**, 606). In substances like this, which have a symmetrical molecule but crystallise in enantiomorphous forms, the configuration (*d*- or *l*-) assumed by any given crystal must be determined by chance. The relative probability of production of *d*- and *l*-crystals might therefore prove easily susceptible of influence by an asymmetric environment. This was found to be the case. When sodium chlorate crystallised from pure water, the numbers of *d*- and *l*-crystals deposited were shown to be equal within the limits of normal variation. Addition of glucose, however, brought about a remarkable disproportion in the numbers of the two forms produced, a large excess of *l*-crystals being deposited. In crystallisations from solutions containing 200 g. of glucose per litre the mean ratio found was 32% of *d*- to 68% of *l*-crystals.

To show that the effect was due to the enantiomorphism of the added glucose and was not directly related to its optical activity a similar series of experiments was carried out with *d*-mannitol, which is practically inactive in aqueous solution. The directive effect of mannitol on the crystallisation of sodium chlorate was found to be at least as great as that of glucose.

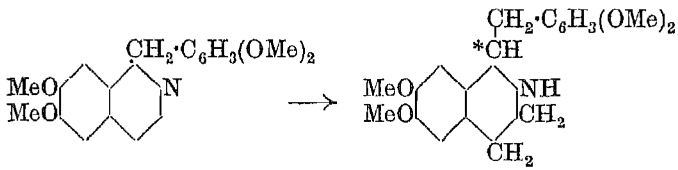
The results of some rather similar experiments on sodium ammonium racemate were not published until several years later (*J.*, 1909, **95**, 103). When aqueous solutions of sodium ammonium racemate were allowed to evaporate spontaneously in open beakers so that only a few large crystals separated, the deposits consisted in the main of sodium ammonium *d*-tartrate, the *l*-tartrate remaining supersaturated in the solution. This preferential deposition of the *d*-tartrate was doubtless due to inoculation of the solution by *d*-tartrate particles present in the laboratory atmosphere, though Kipping and Pope also suggested as a possible alternative cause the presence in the racemate of a minute excess of *d*-tartrate. Deposits consisting of numerous small crystals usually showed little or no activity. Atropine sulphate was subsequently found by Anderson and Hill to show a similar behaviour (*J.*, 1928, 993).

This fruitful partnership was brought to an end by Kipping's appointment to the Professorship of Chemistry at University College, Nottingham, and shortly afterwards Pope went as Head of the Chemical Department to the Goldsmiths' Institute at New Cross.

Goldsmiths' Institute, New Cross. 1897—1901.

Here he threw himself into research with intense activity. He inspired an enthusiastic band of workers—among them S. J. Peachey and A. W. Harvey—and papers poured from his laboratory in a rapid stream.

One of his first investigations—carried out with Peachey—was on the optical resolution of " tetrahydropapaverine " (*J.*, 1898, **73**, 893, 902). Its object was to illustrate the way in which stereochemical methods could be used for the determination of structure. According to the formula which Goldschmiedt had proposed for papaverine (*Monatsh.*, 1888, **9**, 778) the alkaloid itself (in accordance with its optical inactivity) contained no asymmetric carbon atom, but one should be generated in the reduction to tetrahydropapaverine.



The optical resolution of the inactive tetrahydro-derivative would therefore provide confirmatory evidence for Goldschmiedt's formula. Goldschmiedt's " tetrahydropapaverine " was in fact, as was afterwards found by Pyman (*J.*, 1909, **95**, 1610), a dihydro-derivative, but Pope and Peachey showed that it could be resolved and thus made an important contribution to the evidence for its constitution. The resolution was, however, not effected without difficulty and the method by which the solution of the problem was achieved was to lead to far-reaching results.

Till then the only acid employed for the resolution of bases had been tartaric acid, but this proved to be useless for the resolution of " tetrahydropapaverine ", since the crystalline tartrate was homogeneous. It was a partial racemate in which one molecule of *d*-tartaric acid was combined with one molecule of the *d*- and one of the *l*-base.

In seeking a means of getting round this difficulty it was natural that Pope should think of the camphorsulphonic acids with which his earlier work had made him so familiar. They were strong acids, forming stable salts even with weak bases. They were monobasic and thus free from the disadvantages connected with the dibasicity of tartaric acid. Also their salts usually crystallised exceedingly

well. Accordingly the bromocamphorsulphonate of "tetrahydropapaverine" was investigated and was found to be easily resolvable. Chlorocamphorsulphonic acid could also be used for the resolution of the base but was less convenient.

The camphorsulphonic acids were then applied to the resolution of other externally compensated bases. Tetrahydroquinaldine, tetrahydro-*p*-toluquinaldine and *ac*-tetrahydro-β-naphthylamine were all split into optically active components and from each of these investigations some point of general interest emerged.

For the resolution of tetrahydroquinaldine Pope (with Peachey) described a device which he termed "the equilibrium method". It consisted in using enough only of the optically active acid to combine with one of the two components of the externally compensated base, an acid such as hydrochloric being added to combine with the other component. The method was especially effective when the required salt was sparingly soluble.

In connexion with the resolution of tetrahydro-*p*-toluquinaldine a useful procedure was described for surmounting the difficulty of isolating the component which forms the more soluble salt with the resolving agent. It depended on the fact that the component with the more soluble bromocamphorsulphonate not infrequently gave the less soluble salt with Reychler's camphorsulphonic acid. Thus, after separation of the pure *d*-bromocamphorsulphonate of the *l*-base, the mother-liquors were treated with alkali, and the liberated base converted into β-camphorsulphonate. Crystallisation of this readily gave the *d*-base *d*-camphorsulphonate (*J.*, 1899, **75**, 1093).

Finally, in studying the resolution of *ac*-tetrahydro-β-naphthylamine, Pope and Harvey made the surprising observation that extensive optical inversion occurred when salts of the optically active base were treated with alkalis (*J.*, 1901, **79**, 94). There is no evident mechanism by which the inversion could be brought about, for the explanation suggested by Pope and Harvey is scarcely tenable in the light of present knowledge, and the question invites further investigation.

After the efficacy of the camphorsulphonic acids as resolving agents had been established Pope lost no time in applying them to one of the outstanding questions of the day—the possibility of obtaining optically active asymmetric nitrogen compounds. The subject was at that particular time receiving great attention. Marckwald and von Droste-Huelshoff (*Ber.*, 1899, **32**, 560) had just carried out an exceedingly careful examination of Le Bel's claim

(*Compt. rend.*, 1891, **112**, 724) to have obtained an optically active quaternary ammonium salt by growing a micro-organism in a solution of methylethylpropyl*iso*butylammonium chloride and had been entirely unable to confirm his results. Le Bel had quickly replied (*ibid.*, 1899, **129**, 548), amplifying and confirming his former observations. However, many years later Pope and Read (*J.*, 1912, **101**, 519) carried out a very carefully controlled preparation of methylethylpropyl*iso*butylammonium iodide and found Le Bel's description so much at variance with the facts that they were forced to the conclusion that Le Bel never obtained this compound and that the slight optical activity he had observed was to be ascribed to some impurity introduced with, or formed by, the micro-organism.

Besides using biochemical methods, Marckwald and von Droste-Huelshoff had endeavoured to resolve methylethylpropyl*iso*-butylammonium by means of its tartrate, camphorate, and mandelate, but without success. Wedekind also was actively engaged on the same subject (*Ber.*, 1899, **32**, 517). He had prepared a new quaternary ammonium salt containing four different hydrocarbon radicals—benzylphenylallylmethylammonium iodide—but all his attempts to resolve it with the aid of tartaric or camphoric acid had failed.

Pope then, with Peachey's assistance, made benzylphenylallyl-methylammonium iodide by Wedekind's method, converted it into the camphorsulphonate, and immediately found that this was resolvable into diastereoisomers from which the optically active *d*- and *l*-quaternary ammonium iodides and bromides could be prepared, thus proving " that quaternary ammonium derivatives in which the five substituting groups are different, contain an asymmetric nitrogen atom which gives rise to antipodal relationships of the same kind as those correlated with an asymmetric carbon atom " (*J.*, 1899, **75**, 1127; 1901, **79**, 828).

The production of optically active ammonium salts was quickly followed by the resolution of asymmetric compounds of sulphur (Pope and Peachey, *J.*, 1900, **77**, 1072) and of selenium (Pope and Neville, *J.*, 1902, **81**, 1552). The sulphur compound resolved was methylethylthetine bromide, $CO_2H{\cdot}CH_2{\cdot}SMeEtBr$, and the selenium compound the analogous phenylmethylselenetine bromide, $CO_2H{\cdot}CH_2{\cdot}SePhMeBr$, both resolutions being effected by means of bromocamphorsulphonic acid.

The search for a suitable selenium derivative brought out an interesting point in the chemistry of selenium. Phenyl methyl

sulphide is incapable of combining with bromoacetic acid to form a thetine bromide, but Pope suspected that, since thio-ethers are more basic than ethers, selenides might be still more basic, and this proved to be correct, for phenyl methyl selenide was found to combine readily with bromoacetic acid. An increasing tendency to " onium compound " formation in the triad, oxygen, sulphur, selenium, was thus demonstrated.

At the same time he was working with Peachey on the production of optically active asymmetric tin compounds (*Proc.*, 1900, **16**, 42, 116). The problem of finding suitable material was solved by the discovery of an elegant series of reactions by which the trimethyltin iodide of Ladenburg and Cahours could be converted into methylethylpropyltin iodide :

$$\begin{tikzcd} \mathrm{Me_3SnI} \arrow[r, "\mathrm{ZnEt_2}"] & \mathrm{EtMe_3Sn} \arrow[r, "\mathrm{I_2}"] & \mathrm{EtMe_2SnI} \arrow[d, "\mathrm{ZnPr_2}"'] \\ & \mathrm{PrEtMeSnI} & \mathrm{PrEtMe_2Sn} \arrow[l, "\mathrm{I_2}"'] \end{tikzcd}$$

The latter compound was a liquid volatile without decomposition and soluble in non-polar solvents. It thus contained iodine covalently bound, but it gave with silver *d*-camphorsulphonate a camphorsulphonate which was soluble in water and was evidently a true salt. When an aqueous solution of this salt was evaporated to dryness, it was completely converted into *d*-methylethylpropyltin *d*-camphorsulphonate. This was the first recorded example of a phenomenon of which several instances have been since observed—the activation of an easily racemised radical by separation from solution in combination with an optically active complex. On treating the aqueous solution of the activated camphorsulphonate with potassium iodide, dextrorotatory methylethylpropyltin iodide was precipitated. Exactly similar phenomena were observed with the bromocamphorsulphonate. The rotation of the active iodide was variable on account of the ready racemisation, but the investigation gave decisive proof of the optical activity of asymmetric tin.

This series of researches, following one another in such rapid succession, attracted wide attention. The discovery that the valencies of other elements besides carbon had sufficient configurational stability to give observable optical activity in their asymmetrical combinations was immediately recognised as one of the first importance and it gained for Pope an established position in the front rank of scientific investigators.

The work was done at a time when the distinction between electrovalency and covalency was imperfectly understood, and the optically active compounds of quadrivalent sulphur, selenium, and tin were regarded as formally analogous to compounds of asymmetric quadrivalent carbon. Nevertheless Pope fully realised that the compounds were salts and that they must be held to ionise, and he drew attention to the surprising fact that the optically active ions maintained an asymmetric configuration although three radicals only were attached to the central atom (*J.*, 1901, **79**, 840).

The case of tin is, however, fundamentally different from that of sulphur or selenium. The sulphonium and selenonium ions $[SR_3]^+$ and $[SeR_3]^+$ are presumably analogous in electronic structure and in configuration to the phosphine and arsine molecules PR_3 and AsR_3 and these, like ammonia and the amines, are known to be nonplanar. The trialkyltin cation $[SnR_3]^+$, however, would be expected to correspond in configuration with the molecule of a trialkyl derivative of a Group III element and these molecules, like that of boron trimethide, are doubtless planar.

In an ion $[SnR_3]^+$, however, the tin atom would have an incomplete valency shell and, like boron in its 3-covalent compounds, should show a great tendency to co-ordination. It would seem possible, therefore, that Pope and Peachey's camphorsulphonate, prepared in aqueous solution, may have contained a cation of the type $[R_3Sn\leftarrow OH_2]^+$ having a tetrahedral configuration and reacting with an iodide ion, probably with inversion, to give a tetrahedral covalent odide :

$$I^{\ominus} + \left[\begin{array}{l} R \\ R \\ R \end{array}\!\!>\!Sn\leftarrow OH_2\right]^+ \rightleftharpoons \left[I\,Sn\!<\!\!\begin{array}{l} R \\ R \\ R \end{array}\right] + H_2O$$

The physiological activity of some of the compounds employed in these investigations caused a good deal of inconvenience. The vapour of the trialkyltin iodides gave rise to various unpleasant symptoms and on this account the work on optically active tin had to be curtailed and the account of the work was limited to two papers in the Chemical Society's *Proceedings*.

The tenacious odour of the organic selenides was also very troublesome. On Kipping's visits to London he and Pope generally arranged to meet. Professor Kipping says "We usually dined together at Frascati's, but my delight in his company was somewhat tempered by the perfume of the selenium or tellurium compounds with which he had been working and which persisted even after he

had discarded his laboratory clothes. He told me gleefully that when going home from New Cross, even if he started with a full compartment, he would be the sole occupant of the railway carriage before many stations had been passed."

Soon after his appointment to the Cambridge professorship he again began work on selenium. He proposed to prepare the optically active methylethylselenetine bromide in order to compare its molecular rotation with that of methylethylthetine bromide, and thus find the effect of the change in the central atom on the rotatory power of asymmetric molecules otherwise identical.

A mysterious odour soon appeared and pervaded a considerable area of the town. The Borough authorities became gravely concerned, suspecting the newly installed sewerage system. It was all the more unfortunate since the Darwin Centenary celebrations were just about to begin. At length the smell was traced to its source in the University Chemical Laboratory and that evening the discovery was made known in the *Cambridge Daily News* under the head-line "Drains exonerated. Science the Sinner." An expedition was then equipped with the necessary apparatus and Pope and Read, with assistants, proceeded down the Cam beyond Clayhithe and in a lonely meadow by the river carried through the most malodorous stage of the process. But even then the smell could not be kept within bounds and the work had to be abandoned.

Municipal School of Technology, Manchester. 1901—1908.

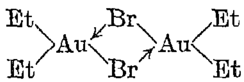
At Manchester Pope's work proceeded at first on the lines which he had been pursuing at New Cross. He completed the work with Neville on optically active selenetines. He continued his studies on the resolution of cyclic bases, with Clark (*J.*, 1904, **85**, 1330) resolving α-methyldihydroindole, which was found to differ from tetrahydro-β-naphthylamine in that there was no racemisation when the salts of the active base were treated with alkali, and with Beck (*J.*, 1907, **91**, 458) employing the α-bromo-β-camphorsulphonic acid of Armstrong and Lowry for a new resolution of tetrahydro-*p*-toluquinaldine in order to show the efficacy of the acid as a resolving agent.

With Peachey he continued the work on the organic compounds of tin and this led to new developments (*Proc.*, 1903, **19**, 290). For the conversion of trialkyltin halides into tetra-alkylstannanes Pope and Peachey had formerly used zinc alkyls. As they had not found them very satisfactory, they now tried instead the organomagnesium

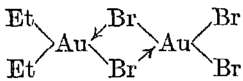
halides discovered a year or two previously by Grignard. These proved far more convenient and effective than zinc alkyls and by following up this observation they were led to discoveries of much interest.

By treating platinic chloride with methylmagnesium iodide they succeeded in obtaining a series of organo-metallic derivatives of platinum (*J.*, 1909, **95**, 571) and, in a similar manner, Pope and C. S. Gibson prepared from auric chloride alkyl derivatives of gold (*J.*, 1907, **91**, 2061). Thus for the first time it was shown that noble metals were capable of combining with alkyl radicals and Pope and Peachey's platinum derivatives are still the only compounds known in which a transitional element is linked to alkyl groups.

The platinum compounds were of the type Me_3PtX, where X was a negative radical such as iodine or NO_3. The gold compounds had the empirical formulæ Et_2AuBr and $EtAuBr_2$, but Gibson and his co-workers subsequently showed that these formulæ must be doubled to give the molecular formulæ, the substances having the constitutions :



and



Conspicuous among the scientific publications issuing from Pope's laboratory during this period were the elaborate memoirs on the relations between chemical constitution and crystal structure in which W. Barlow and he developed the theory generally known as the valency-volume theory of crystal structure (*J.*, 1906, **89**, 1675; 1907, **91**, 1150; 1908, **93**, 1528 : 1910, **97**, 2308). Barlow had long been interested in the geometrical problems presented by the packing of spheres on account of their relation to the arrangement of atoms in crystals. As far back as 1883 he had discovered the two ways—the cubic and the hexagonal—in which equal spheres could be arranged in closest packing. In 1906 he and Pope made the new hypothesis that the space which an atom occupies in a crystal is proportional to its valency. Using this hypothesis in combination with the principle of close packing, taking also into account the information obtainable from crystallographic examination, they endeavoured to deduce the crystal structure of many typical substances. In earlier attempts to gain an insight into the structure of crystals the lattice points had been supposed to correspond with the chemical molecules. In the Barlow-Pope method of approach

atoms were centred on the lattice points and the close-packed assemblage of atoms was then partitioned into molecules.

Although the postulate of the proportionality of volume and valency cannot now be maintained, there was much in these memoirs which foreshadowed present views of crystal structure based on the knowledge gained through *X*-ray analysis. This is true particularly with regard to substances like the metallic elements and the alkali-metal halides in which the valency forces are non-directional and the arrangement of the atoms in the crystals is largely determined by the requirements of close packing.

The outstanding investigation initiated in the Manchester period was that on methyl*cyclo*hexylideneacetic acid. The conception of the asymmetric carbon atom was so easily applicable and had proved so sure a guide in dealing with mirror-image isomerism that in the minds of many organic chemists it had come to overshadow the fundamental principle of molecular dissymmetry on which it had been based. Pope conceived the brilliant idea of producing a compound which should be optically active and yet contain no asymmetric carbon atom in its molecule—at least, none in the ordinary sense. To realise this idea he devised a molecular type which might be regarded as derived from a disubstituted allene (III) by expansion of one of the ethylene residues into a *cyclo*hexane ring.

$$\begin{matrix}R\\H\end{matrix}\!>C{=}C{=}C<\!\begin{matrix}R'\\H\end{matrix} \qquad\qquad \begin{matrix}CH_3\\H\end{matrix}\!>C<\!\begin{matrix}CH_2\cdot CH_2\\CH_2\cdot CH_2\end{matrix}\!>C{=}C<\!\begin{matrix}CO_2H\\H\end{matrix}$$

(III.) (IV.)

With convenient substituents this gave methyl*cyclo*hexylideneacetic acid (IV). Although in this compound no carbon atom is attached to more than three unlike atoms or groups, a tetrahedral arrangement of the carbon valencies makes its molecule non-superposable upon its mirror-image. It should therefore exist in two enantiomorphous modifications.

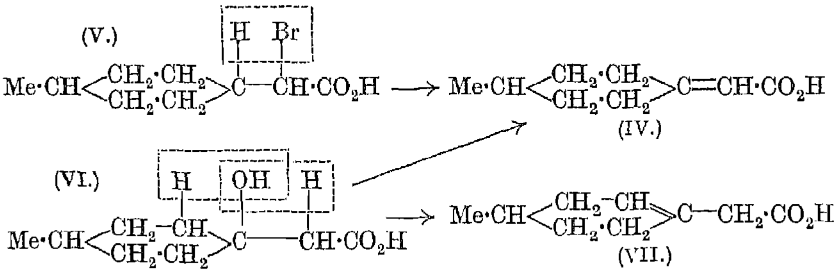
For the production of this compound he secured the collaboration of W. H. Perkin, who then occupied the chair of Organic Chemistry in the University of Manchester, and a process for its synthesis was described in a joint paper in 1908 (*J.*, 1908, 93, 1075), a preliminary account having been published in 1906.

By a remarkable coincidence Marckwald and Meth were at the same time engaged on the synthesis of this very compound for the same purpose (*Ber.*, 1906, 39, 1171, 2404). They prepared an acid which they believed to be methyl*cyclo*hexylideneacetic acid and

succeeded in resolving it into optically active components. It was, however, different from Perkin and Pope's acid.

Perkin and Pope's acid was obtained by the elimination of hydrogen bromide from the compound (V). The elimination could take place in one way only and the constitution of the acid was therefore definitely fixed by its synthesis. Perkin and Pope's acid was unquestionably methyl*cyclo*hexylideneacetic acid (IV).

Marckwald and Meth's acid was obtained by the elimination of water from the compound (VI). This substance could lose water in two ways, forming a double bond either in the semicyclic position (IV) or in an endocyclic position (VII). Since the resulting compound was different from Perkin and Pope's acid, the elimination



must have taken place in the second way (notwithstanding evidence obtained by Marckwald and Meth which, superficially considered, seemed to indicate that the double bond was in the semicyclic position). Marckwald and Meth's acid was therefore methyl*cyclo*hexeneacetic acid (VII). This compound contains an ordinary asymmetric carbon atom and no special interest attaches to its resolution.

Although Perkin and Pope's process gave the right acid, it involved several difficult operations and it could not easily be made to yield enough of the substance for resolution. Shortly afterwards, however, Wallach in Göttingen chanced on a simpler synthesis. He found that the way in which water was eliminated from β-hydroxy-acids of the type (VI) depended on the nature of the dehydrating agent used. Strongly acid dehydrating agents like potassium bisulphate, phosphoric oxide, or the dilute sulphuric acid used by Marckwald and Meth, led to the formation of a double bond in the endocyclic position. Acetic anhydride, on the other hand, gave a semicyclic double bond. Methyl*cyclo*hexylideneacetic acid could

therefore be obtained with comparative readiness by heating the compound (VI) with acetic anhydride.

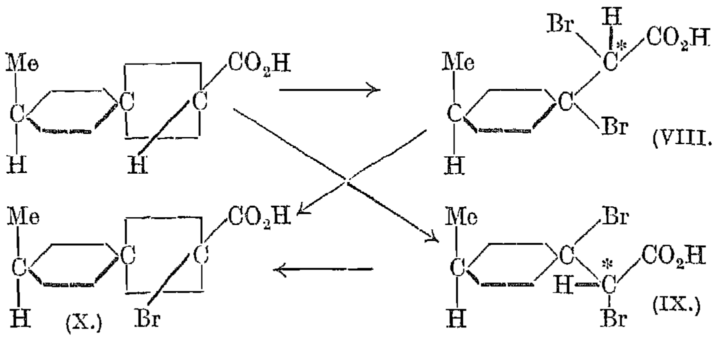
Wallach thereupon informed Perkin that he had got a method by which the acid could be made in quantity. He was not prepared to divulge the method, but he sent Perkin some of the acid and in return his name was to be included in the title of the paper.

On December 18th, 1908, Perkin wrote to Pope, then established at Cambridge: "The whole of the acid (now about 25 grams, originally 30 grams) I have sent on to you for you to see whether you can get anything optically active out of it. If not, the question arises, What other differences may the two enantiomorphous modifications possibly exhibit and how can we prove these experimentally? The problem must surely be a very interesting one whichever way it goes." The solution of the problem was not long in coming. The acid was shown to be resolvable into optically active components. This final realisation of Pope's idea was accomplished with the assistance of Dr. John Read, now Professor of Chemistry at St. Andrews, and the rotatory power of the active modifications of the acid proved to be quite considerable ($[\alpha]_D \pm 81°$). The resolution presented unusual difficulty. The salts of the acid with the alkaloids and other optically active bases showed the greatest reluctance to crystallise * and when the brucine salt had at length been obtained crystalline the separation of the salts of the *d*- and *l*-acids was greatly impeded by their mutual solubility in the solid state. By an exceptional arrangement the account of the resolution was published simultaneously in English and in German (*J.*, 1909, **95**, 1789; *Annalen*, 1909, **381**, 180).

In a later paper (*J.*, 1911, **99**, 1510) Perkin and Pope described further work on the acid, in which, among other reactions, transformations of the "centroasymmetric" compound into compounds containing an ordinary asymmetric carbon atom were studied. Thus, the addition of bromine to the optically active *cyclo*hexylidene

* Professor Read relates how the accomplishment of this exceptionally difficult task was helped by the remissness of a laboratory attendant. The boy neglected an instruction to clean up an accumulation of watch-glasses containing the results of many seemingly unsuccessful experiments and after two or three days he was sent for to be reprimanded. The glasses had stood, some of them for months, without any sign of crystallisation having been observed, but while awaiting the boy's arrival Read noticed a white speck in a glass containing a glassy film of brucine salt. The speck proved to be crystalline. It was effective in starting the crystallisation of the brucine salt in mass and thus it led ultimately to the resolution.

acid produced two optically active dibromo-acids (*cis-trans* isomerides, VIII and IX).



(VIII.) (IX.) (X.)

In these the molecular dissymmetry arises entirely from the newly formed asymmetric carbon atom C* (on the usual assumption of free rotation about a single bond) and the *cyclo*hexane ring is only concerned (through its 1 : 1 : 4-substitution) in the geometrical isomerism.

The rotations of the two dibromo-acids were found to be of opposite signs. The diagrams show how this probably comes about. Provided that the addition of bromine takes place in a corresponding manner (*i.e.*, by *cis*-addition or by *trans*-addition) in each case, the system $R\cdot CHBr\cdot CO_2H$ will have opposite configurations in the two isomerides. The diagrams are drawn on the assumption of *trans*-addition.

The isomeric dibromo-acids could be transformed back again into a centroasymmetric compound, for with potassium hydroxide they showed the normal behaviour of $\alpha\beta$-dibromo-acids, hydrogen bromide being eliminated with the formation of the α-bromo-$\alpha\beta$-unsaturated acid (X). Both dibromo-acids gave the same optically active methyl*cyclo*hexylidenebromoacetic acid and the rotation of the latter had the same sign as that of the original centroasymmetric acid.

Cambridge. 1908—1939.

In the period following the investigations on methyl*cyclo*hexylideneacetic acid Pope's work was chiefly centred on the stereochemistry of compounds of simple molecular constitution.

The question whether the simpler carbon compounds were capable of showing optical activity was first raised by Eiloart in his translation of van 't Hoff's "Arrangement of Atoms in Space" (1898, p. 25). Eiloart pointed out that in every optically active compound then known at least two other carbon atoms were directly linked to the asymmetric carbon atom, C–C*–C. There was therefore no experimental evidence that asymmetric compounds with less than three carbon atoms in the molecule could show optical activity and he suggested that in these simple compounds the radicals might be too mobile to permit the activity to be observed.

The question of the optical stability of simple molecules then seemed to Pope one of the most important unsolved problems of stereochemistry and he had already begun to work on it at Manchester. There, with Read, he had prepared chlorosulphoacetic acid, $CHCl(CO_2H)\cdot SO_3H$, and chlorobromomethanesulphonic acid, $CHClBr\cdot SO_3H$, both described by Andreasch in 1887, and had tried to resolve them. A number of crystalline salts with optically active alkaloids were obtained but none of them had proved resolvable (*J.*, 1908, **93**, 794).

This failure might have been due, either to the mobility of the groups in these simple molecules, or to a special tendency of the alkaloidal salts of the simpler asymmetric acids to form partial racemates. Since he thought that the power to form partial racemates might occur less frequently in non-ionic compounds than in salts, Pope examined the possibility of avoiding the formation of these combinations by using non-ionic diastereoisomeric derivatives instead of diastereoisomeric salts for effecting resolutions.

With this object he and Read studied the condensation products (XI) which oxymethylenecamphor forms so readily with primary and secondary bases:

$$C_8H_{14}\Big<\begin{array}{l}C{:}CH\cdot OH\\CO\end{array} \xrightarrow{R\cdot NH_2} \underset{\text{(XI.)}}{C_8H_{14}\Big<\begin{array}{l}C{:}CH\cdot NHR\\CO\end{array}} \xrightarrow{Br_2} C_8H_{14}\Big<\begin{array}{l}CBr\cdot CHO\\CO\end{array} + R\cdot NH_2,HBr$$

They examined a number of such products and found that externally compensated bases could in fact be resolved by means of them. *dl*-α-Phenylethylamine, for example, gave with *d*-oxymethylenecamphor two diastereoisomerides separable by fractional crystallisation, and from the separated diastereoisomerides the two enantio-

morphous optically active bases could be obtained (*J.*, 1909, **95**, 171; 1913, **103**, 444).

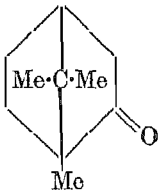
To regenerate the active bases from the condensation products an effective method was discovered consisting in treatment with bromine. Smooth fission into bromoformylcamphor and the hydrobromide of the base was thus brought about and by this device the process was made a practically useful method for resolving bases (*J.*, 1912, **101**, 2337).

Further investigation showed, however, that it afforded no escape from partial racemism. When applied to the resolution of *dl*-tetrahydro-*p*-toluquinaldine, it failed (*J.*, 1913, **103**, 1515). The *d*-methylenecamphor derivative of this base was not separable by fractional crystallisation into its diastereoisomeric components and the cause was the formation of a partial racemate. By combining the *d*- and the *l*-form of the base (readily obtained by resolution with bromocamphorsulphonic acid) with *d*- and with *l*-oxymethylenecamphor the four possible stereoisomeric forms of the condensation product were prepared and their crystalline combinations were studied in detail. Suitably paired, they gave not only the two fully racemic forms, but also four partial racemates, since *d*B*d*C (B representing the residue of the base and C that of methylenecamphor) formed crystalline combinations with both *l*B*d*C and *d*B*l*C, and the mirror images of these two combinations were of course formed by *l*B*l*C. Tetrahydro-*p*-toluquinaldinomethylenecamphor was thus shown to exist in no less than ten different crystalline stereoisomeric forms. These were all obtained in a state of purity and the investigation is probably the most complete study yet made of the racemic relationships of a pair of diastereoisomerides and their mirror images.

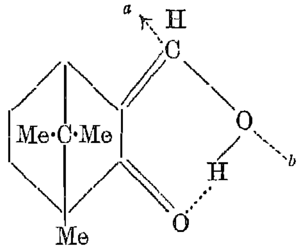
Since the molecular solubility of the individual diastereoisomerides was greater than that of any of their crystalline combinations, neither the base nor oxymethylenecamphor could be resolved by fractional crystallisation of their condensation product. The optically active forms of the base could nevertheless be obtained by means of oxymethylenecamphor in another way. *d*-Oxymethylenecamphor was found to react so much more rapidly with *l*- than with *d*-tetrahydro-*p*-toluquinaldine that the difference could be used for the resolution of the base.

It may be remarked that through this difference in reaction velocities it should be possible to relate the configurations of *d*- and *l*-camphor to those of *d*- and *l*-tetrahydro-*p*-toluquinaldine. The difference is evidently due to unequal steric hindrance arising

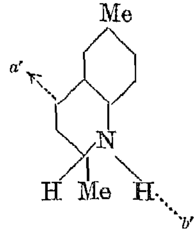
from the relative orientations of the α-methyl group of the base and the *gem*-dimethyl group of oxymethylenecamphor:



(XII.)



(XIII.)



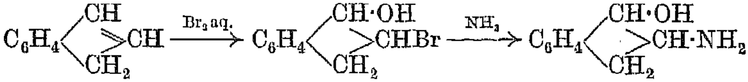
(XIV.)

If, in order to interact, the two molecules must (as would appear necessary) have the axes *ab* *a′b′* similarly directed, then it seems evident that (XIV) represents the form of tetrahydro-*p*-toluquinaldine in which the methyl group is so oriented as to cause the greater hindrance to interaction with the form (XIII) of oxymethylenecamphor.* Hence, if (XII) is *d*-camphor, (XIV) is the form of the base which reacts the more slowly with *d*-oxymethylenecamphor, *viz.*, *d*-tetrahydro-*p*-toluquinaldine.

Since non-ionic diastereoisomerides could thus possess in a high degree the power to form partial racemates, it seemed unlikely that their use in place of salts would prove generally advantageous in resolutions. Pope therefore looked for other methods of resolving acids.

Though many more bases were available for resolving acids than acids for resolving bases, yet no base was known which was comparable in efficiency with the camphorsulphonic acids. He accordingly tried to find an optically active base which would correspond in effectiveness with these acids—that is to say, a base of great strength, giving salts of great crystallising power, and at the same time sufficiently easily obtainable.

With this object he and Read examined hydroxyhydrindamine, readily prepared from indene by the following reactions:



This compound was found to possess in a considerable degree the properties required. It was a strong organic base—strong enough

* The heavy lines in formulæ XII—XIV represent bonds inclined *towards* the reader.

to form a stable carbonate—most of its salts crystallised well and it was easily resolved with bromocamphorsulphonic acid (*J.*, 1911, **99**, 2071; 1912, **101**, 758).

Its active forms were at once applied to the resolution of acids with simple molecules and they speedily brought success. The first experiments, made on chlorobromomethanesulphonic acid, already gave indications that a resolution was being effected. To ensure more favourable conditions a new acid of somewhat more promising constitution, chloroiodomethanesulphonic acid, was prepared and with this compound resolution was definitely achieved. Though the possibility of its resolution was first established with *l*-hydroxyhydrindamine, it was found afterwards that resolution could also be effected—and more completely—by fractional precipitation of the very sparingly soluble brucine salt. The active acid showed a considerable molecular rotation $[M]_{5461} + 43°$ and its optical activity proved to be remarkably stable, since its aqueous solution could be boiled, even with the addition of ammonia—and indeed even heated for 2 hours at 130—150°—without loss of activity (*J.*, 1914, **105**, 811).

Thus it was proved that a compound having only a single carbon atom in its molecule could exist in a stable optically active state. This substance contains less than 5% of carbon and there are only 9 atoms in its molecule; in the optically active anion there are but 8 atoms, only 3 more than the minimum number required for the formation of a dissymmetric carbon compound.

This discovery filled an important gap in the stereochemistry of carbon. It also removed the basis of Eiloart's suggestion that one- and two-carbon compounds were configurationally unstable. There is no theoretical justification for this suggestion. The evident reason why optically active one- and two-carbon compounds had not been obtained before was the difficulty of finding compounds suitable for resolution among the small number of molecularly dissymmetric substances in these classes.

Of the few molecularly dissymmetric compounds which they contain, some like ethylidene chlorobromide belong to types to which the usual methods of resolution are inapplicable, others like aldehyde-ammonia are unstable towards resolving agents, while others like chlorobromoacetic acid and chlorosulphoacetic acid (which, however, have subsequently been resolved) present special difficulties on account of the readiness with which they racemise, the racemisation being due, not to the kind of mobility suggested by Eiloart, but to

the presence of an α-hydrogen atom rendered specially prone to prototropic change by the presence of two substituent halogen atoms, or of a halogen atom and a sulpho-group, in addition to the carboxyl.

In his selection of chloroiodomethanesulphonic acid Pope's sure instinct was shown, for in the light of present knowledge it would seem that there could hardly be any compound better suited to his purpose

Soon after this work was completed he left for Australia to attend the Australian meeting of the British Association as President of Section B (Chemistry). His presidential address, delivered in Melbourne, showed his strongly maintained interest in the Barlow-Pope theory of crystal structure. The address began with an outline of recent progress in stereochemistry, but at least two-thirds of it were devoted to the valency-volume theory. The first results of *X*-ray analysis had then just been obtained and he was able to compare the experimentally ascertained structures of diamond and rock-salt with the predictions of the theory.

During the Australian meeting war was declared and after his return to Cambridge Pope became actively engaged on chemical problems arising out of the national emergency, calling on the co-operation of most of the staff of the University Chemical Laboratory. He rendered assistance in many directions, more especially in connection with the sources of high explosives, aerial photography, and retaliation to the German use of poison gases. Many of the results of these researches were of considerable scientific interest and were published after the end of the war. Notable among them were the investigations carried out with C. S. Gibson (*J.*, 1920, **117**, 271) on the action of sulphur chlorides on ethylene—a subject first studied by Guthrie in 1860. As a result of these researches it was shown that an almost quantitative yield of dichlorodiethyl sulphide could be obtained by the strongly exothermic reaction

$$2C_2H_4 + S_2Cl_2 = (C_2H_4Cl)_2S + S$$

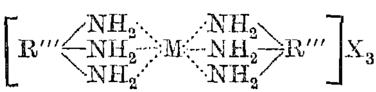
Several other investigations on dichlorodiethyl sulphide were carried out in the immediate post-war period and one of these, carried out with F. G. Mann, had very interesting consequences. In connexion with the use of chloramine-T as an antidote to mustard gas it had been found by H. S. Raper that dichlorodiethyl sulphide gave a crystalline condensation product with sodium toluene-*p*-sulphonchloroamide :

$$(C_2H_4Cl)_2S + {}^{Na}_{Cl}{>}N{\cdot}SO_2{\cdot}C_7H_7 = (C_2H_4Cl)_2S{:}N{\cdot}SO_2{\cdot}C_7H_7 + NaCl$$

Pope and Mann now showed that the power to react in this manner with salts of aromatic sulphonchloroamides was a very general property of dialkyl sulphides and for the resulting condensation products they proposed the name sulphilimine (*J.*, 1924, **125**, 911). Pope regarded the nitrogen–sulphur link formed in this condensation as analogous to the nitrogen–carbon link in the oximes, *i.e.*, as a 4-electron bond. Kenyon and Phillips, however, subsequently resolved sulphilimines derived from unsymmetrical sulphides into optically active components, thus showing that the link was a semipolar or co-ordinate (*i.e.*, a 2-electron-) link.

After normal conditions had been restored Pope turned again to stereochemistry, entering what was for him a new province—that of the co-ordination compounds of the metals.

When an aliphatic diamine co-ordinates with a 6-co-ordinating metal, the full number of isomers required by an octahedral configuration of the complex can in many cases be obtained. Pope proposed to extend the development of this subject by studying the co-ordination compounds of the aliphatic triamines. Since compounds of the annexed type should exist in three stereoisomeric forms, of which one should be resolvable into optically active enantiomorphs, this seemed to offer a rich field for investigation and its experimental exploration was undertaken with the assistance of F. G. Mann. The expected isomerism could not, however, be realised. The first trials were made with the simplest triamine, triaminopropane, $NH_2{\cdot}CH_2{\cdot}CH(NH_2){\cdot}CH_2{\cdot}NH_2$, and several cobaltic and rhodium derivatives of the type $[M.trp_2]X_3$ were prepared, but none could be obtained in more than one form (*Proc. Roy. Soc.*, 1925, *A*, **107**, 80).



Triaminotriethylamine $N(CH_2{\cdot}CH_2{\cdot}NH_2)_3$ was then examined (*Proc. Roy. Soc.*, 1925, *A*, **109**, 444). Since tertiary bases like triethylamine do not form metallic co-ordination compounds, it seemed probable that only the three amino-groups would co-ordinate so that this comparatively accessible base could be used for the study of triple co-ordination. Actually, however, all four nitrogen atoms proved able to co-ordinate, and with metals capable of 6-co-ordination compounds of the types $[Ni_2\,tren_3]X_4$ and $[Cl_2Pt\,tren]X_2$ were formed, whilst with 4-co-ordinating metals compounds like $[Ni\,tren]SO_4$ and $[Pd\,tren]I_2$ resulted. Although it would appear that the complex $[Ni_2\,tren_3]^{IV}$ must necessarily be dissymmetric, it

could not be resolved, possibly, as Pope and Mann suggested, on account of its rapid racemisation.

The analogous base triaminotripropylamine,

$$N(CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}NH_2)_3,$$

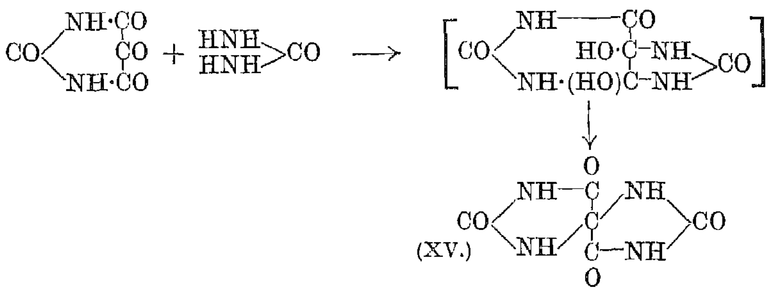
was also synthesised and was likewise found to co-ordinate as a tetramine, giving compounds with nickel of the type [Ni trpn]X_2 (*J.*, 1926, 489).

Whilst the primary object of the work thus could not be attained, various points of interest in connexion with co-ordination emerged from it. One of these concerns the configuration of the 4-co-ordinated nickel atom. Triaminotriethylamine was found to yield the nickel derivative $\left[N[C_2H_4{\cdot}NH_2]_3{\equiv}Ni\right]SO_4$, for which the simple molecular weight was established (*J.*, 1926, 482). If the nickel valencies have the normal planar arrangement, the production of this compound clearly entails great intramolecular strain, but if they are tetrahedrally arranged, it would be strainless. A knowledge of its actual configuration is therefore much to be desired.

Another point of interest concerns the manner in which triaminopropane co-ordinates with platinic chloride (*J.*, 1927, 1224). Interaction of the triamine with hydrochloroplatinic acid yields a product containing in its molecule 5 atoms of chlorine, of which one is ionic. It is therefore of the type $Cl_4Pt{<}(NH_2)_2C_3H_5{\cdot}NH_3Cl$, derived from the electrically neutral diamminotetrachloroplatinum $[(NH_3)_2PtCl_4]$. The relation between the two amino-groups co-ordinating with the platinum was established by showing that the compound was resolvable into optically active enantiomorphs. This proved that the co-ordination takes place unsymmetrically, *i.e.*, that α- and β-groups co-ordinate with the platinum and the γ-amino-group with the proton, $Cl_4Pt{<}\begin{matrix}NH_2{\cdot}CH{\cdot}CH_2{\cdot}NH_3Cl \\ NH_2{\cdot}CH_2\end{matrix}$. Thus of the two possible structures which might result from the co-ordination—the 5-ring and the 6-ring—the former is in fact produced. This accords with the conclusion to be drawn from a consideration of the relevant atomic radii and intervalency angles. The authors described this as the first recorded case of a carbon atom owing its asymmetry to the operation of auxiliary valencies.

Pope then returned to the stereochemistry of centroasymmetric substances and started investigations which led to the discovery of two particularly elegant examples of optically active compounds of the spirocyclic class. The first of these was *spiro*-5 : 5-dihydantoin

(XV). *spiro*-Dihydantoins were obtained long before their constitution became known. Trimethyl*spiro*dihydantoin was encountered by Emil Fischer in 1882 in his classical investigation on caffeine: it was his hypocaffeine. He had mistaken its nature, regarding it as a 7-carbon- instead of, as it actually was, an 8-carbon-compound. Later he obtained also the tetramethyl derivative but did not discover its constitution, naming it oxytetramethyluric acid. The true nature of these compounds was first recognised by H. Biltz after his discovery of the uric acid glycols. He saw that they were spirocyclic compounds formed through intermediary unstable uric acid glycols by an intramolecular change resembling the pinacone transformation. He confirmed this view by synthesising the parent compound from urea and alloxan, thus at the same time providing a convenient method for its preparation.



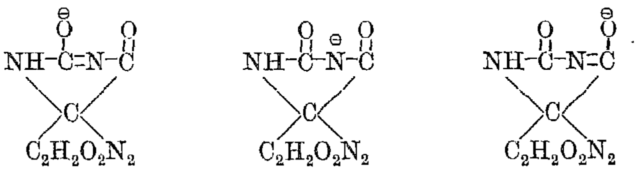
(XV.)

Pope's attention was attracted to this substance as a centroasymmetric compound of particularly simple constitution and he perceived that it would be sufficiently acidic to form salts with alkaloids. With J. B. Whitworth (*Proc. Roy. Soc.*, 1931, *A*, 134, 357) he showed that it could be in fact resolved with brucine with surprising readiness, the hot alcoholic solution of the di-brucine salt depositing the *l*-form nearly quantitatively as monobrucine salt on cooling, whilst the mother-liquor deposited the *d*-form as dibrucine salt on standing. It may well be that this substance, having not more than one exocyclic atom on any ring-member, is the simplest centroasymmetric spirocyclic compound that will ever be obtained in optically active forms.

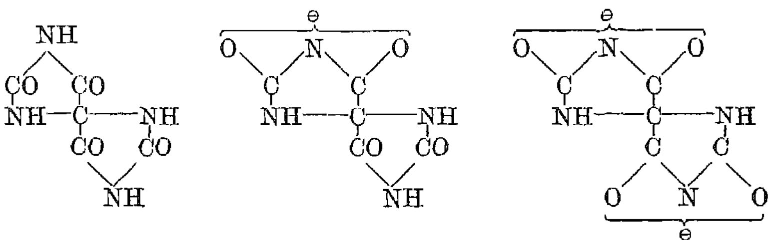
In view of the tautomeric possibilities associated with the presence of –CO·NH– groupings the precise structure of the dihydantoin is not easily established and the interest attaching to its optical activity depends on both rings being similarly constituted, for otherwise an

ordinary asymmetric carbon atom would be present. There can, however, be little doubt that the compound actually has the lactam structure (XV) and Pope and Whitworth (*Proc. Roy. Soc.*, 1936, *A*, **155**, 1) saw confirmation of this in the close relation which they found between its rotatory dispersion and that of its tetramethyl derivative formed by the action of diazomethane on the active dihydantoin, the ratio of the molecular rotations of the two compounds being almost constant over the range of wave-lengths examined. (The methyl groups in the tetramethyl derivative are known to be on the nitrogen atoms.)

When the *d*-dihydantoin is dissolved in aqueous sodium hydroxide (1 mol.), the rotatory power falls to roughly one half. The addition of a second molecular proportion of sodium hydroxide produces a further fall in the rotation, the solution then becoming lævorotatory. Pope and Whitworth considered that these changes of rotatory power indicated passage to tautomeric enolic forms. The molecular species whose rotations are observed under these conditions are, however, the univalent and bivalent anions and these would now be regarded as resonance hybrids, the normal state of the univalent ion corresponding with resonance between the three structures



whilst in the bivalent ion such resonance would occur in both rings. The relation between structure and rotatory power $[\alpha]_{5461}$ in these substances in aqueous solution is as follows:



+ 112° + 59° − 6°

The second of the two spirocyclic compounds resolved was diamino*spirocyclo*heptane (XVI). Many years previously, immedi-

ately after completing the work on methyl*cyclo*hexylideneacetic acid, Pope and Read had made experiments on the resolution of the *spirocyclo*heptanedicarboxylic acid (XVII) obtained by Fecht in 1907 from pentaerythritol.

$$\text{(XVI.)}\quad NH_2{\cdot}CH{<}^{CH_2}_{CH_2}{>}C{<}^{CH_2}_{CH_2}{>}CH{\cdot}NH_2$$

$$HO_2C{\cdot}CH{<}^{CH_2}_{CH_2}{>}C{<}^{CH_2}_{CH_2}{>}CH{\cdot}CO_2H\quad \text{(XVII.)}$$

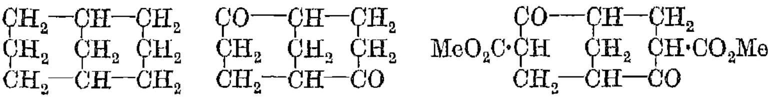
Just as methyl*cyclo*hexylideneacetic acid could be regarded as derived from a disubstituted allene by the expansion of one double bond into an alicyclic ring, this acid might be considered to be derived by the expansion of both the allene double bonds into *cyclo*butane rings.

Pope and Read obtained products showing some optical activity, but the rotatory power observed was so small that the results were not published. Twenty years later (in 1931) Backer and Schurink published an account of the resolution of this acid in which the molecular rotation recorded ($[M]_D + 1{\cdot}9°$ in ether) was of the same order as that which Pope and Read had observed. Pope then perceived that the diamine corresponding to (XVII) was likely to provide more favourable material for demonstrating the dissymmetry of this molecular type. Accordingly, with S. E. Janson (*Chem. and Ind.*, 1932, 316) he replaced the carboxyl groups in Fecht's acid by amino-groups, using K. F. Schmidt's newly patented method of treatment with azoimide in concentrated sulphuric acid solution. The new base thus obtained could be readily resolved by means of camphor-β-sulphonic acid into enantiomorphous forms of considerable optical activity (the hydrochloride had $[M]_{4358} \pm 30°$ in aqueous solution), a result which gave Pope much satisfaction.

On account of the rigidity and the simplicity of its molecule this compound is well adapted for the application of mathematical theories of optical rotatory power and it was so employed by Born (*Proc. Roy. Soc.*, 1935, *A*, **150**, 84). The close relationship in constitution between diamino*spirocyclo*heptane and *spirocyclo*heptanedicarboxylic acid together with the tendency of enantiomorphous molecules to crystallise together to form racemates might suggest that the optically active base would form a considerably less soluble salt with the acid of unlike than with that of like configuration, so that the active base would be specially effective in resolving the *dl*-acid.

This was, however, not so; the acid proved to be non-resolvable by the active base.

The last research which Pope undertook was an investigation of derivatives of *bicyclo*-[1 : 3 : 3]nonane (XVIII), some of which, if they could be prepared, would be of considerable stereochemical interest. The diketone (XIX) represents a type of molecular dissymmetry not



(XVIII.) (XIX.) (XX.)

yet realised and the hydrocarbon itself is of interest since its nine carbon atoms should be capable of assuming an arrangement identical with a section of the crystal lattice of diamond. The work was begun with the assistance of Janson and the crystalline methyl ester (XX) was obtained in an optically active form, but Janson left to take up another appointment and the investigation was never completed.

Of the great body of work which Pope accomplished, nearly the whole was thus concerned in one way or another with molecular configuration, opening up new fields of stereochemistry and enriching others. His discoveries of optically active compounds of nitrogen, sulphur, selenium, and tin, and his pioneer work on centroasymmetric substances will always remain landmarks in the history of the science.

In his Melbourne address he depicted stereochemical investigation as an artistic pursuit—demanding of its followers originality of conception, intuitive choice of material, and practical sense—and in this scientific artistry he was himself a master unsurpassed.

GILBERT THOMAS MORGAN

1870—1940

GILBERT THOMAS MORGAN was born on October 20th, 1870 his father being Welsh and his mother French-Swiss. His early years were spent at Essendon in Hertfordshire, and here was fostered an appreciation of country things which he retained throughout his life. He was never ashamed of the filial and family pieties that our time tends to disparage and weaken. In later years, in spite of the great and increasing demands made upon him, he visited with regularity his aged and blind father, who still resided at Essendon, and from whom he undoubtedly derived a full measure of characteristic Celtic enthusiasm and imagination.

Morgan was educated at the Central Foundation School, Cowper Street, in the City of London, and in 1886 entered the Finsbury Technical College, which had been established in 1878 by the City and Guilds of London to teach science with a practical bias. The training which Morgan received here during the formative years profoundly influenced his scientific outlook. It could not be otherwise. At Finsbury at that time was the somewhat shy and versatile Professor, Raphael Meldola, who was assisted by that gifted teacher of organic chemistry, Frederick William Streatfeild, and by J. Castell-Evans—a striking figure and personality—responsible for the teaching of inorganic chemistry. How well these men moulded the splendid material which came into their hands is reflected in the careers of the many distinguished Finsbury men. A very important factor in the success of the Finsbury training was not only the kind of instruction given but the early emphasis laid upon the practical applications of much of the work done. This made an abiding impression on Morgan, who always had a pronounced sense of practical values. Further, as the Finsbury training engendered self-reliance and evoked a spirit of enquiry and enterprise, the environment must have been particularly congenial to a student of Morgan's calibre. The great interest which Morgan always displayed in the rare earths goes back to this period, for under the guidance of Castell-

G. T. Morgan.

Evans he spent an Easter vacation isolating ceria from the mineral cerite. He records that "this practical exercise imbued me with an attraction for the rare earths which I was able to cultivate further in later years". His first introduction to research took place at Finsbury in the private laboratory of Professor R. Meldola, F.R.S., and one of the topics they studied was the action of concentrated nitric acid on azonaphthols and their ethyl derivatives. They found that the concentrated acid ruptured the azo-linking, regenerating the diazonium salt; the naphthol residue became nitrated. This work was carried out in 1889. In 1905 a German chemist, O. Schmidt, took up this nitric acid treatment of azo-compounds and developed a process for diagnosing azo-dyes which is sometimes known as Schmidt's method.

At the end of his College career Morgan secured a post under Mr. Robert Holliday, the youngest son of Read Holliday, the founder of the well-known firm of colour-makers at Huddersfield. Here he was confronted with problems in both organic and inorganic chemistry, but amongst all the investigations that he undertook, one in particular made an indelible impression. Morgan was deputed to find out whether a new colour-intermediate could be prepared by the condensation of formaldehyde and phenol. A condensation product was obtained, but as it refused to yield dyes it ceased to be of any further interest to his employers. However, it was set aside, and gradually solidified to a clear amber resin. Forty-six years later, in an address to the Society of Chemical Industry, Morgan made the very human confession: "I often think of the contents of that bottle which contained the potentialities of fortune, although we did not perceive it at the time". Baekeland's patents, it will be recalled, dated from about 1906. It was during this period at Read Holliday's that Morgan first developed a keen interest in autoclaves and chemical reactions carried out at high pressures. He relates how he borrowed from a colleague a laboratory autoclave in order to hydrolyse α-naphthonitrile with alkali under pressure. The ammonia generated in the process attacked the copper gauge, ultimately perforating it and rendering it useless. After this experience, the study of autoclaves seemed worth while.

In 1894 Morgan took a bold decision. He decided, with some reluctance, to give up his industrial career and resume his scientific studies. With this end in view he secured a Royal Scholarship and entered the Royal College of Science, London, where he was destined to spend many happy and successful years first as student, later as

demonstrator, lecturer, and finally assistant-professor. In view of his exceptional chemical attainments he did not follow the usual course of study, but was soon assisting Professor William A. Tilden, F.R.S., with various research projects. In 1896 he graduated B.Sc. (London) with first-class honours in chemistry and gained the Frank Hatton Prize of the College, where he continued as a demonstrator and research worker. Morgan now began with characteristic energy and success a programme of research work which during the ensuing years covered such a wide field. His first step was to resume certain investigations which had aroused his interest at Read Holliday's, viz., *condensation of aldehydes and aromatic amines* and studies of aromatic compounds containing nitrogen. In conjunction with several co-workers, especially Miss F. M. G. Micklethwait, he published a series of papers, several of which dealt with diazonium compounds and non-aromatic diazonium salts. Morgan's interest was also aroused at this period by the residual affinity of coumarin in forming salts with inorganic acids and further by the organic derivatives of phosphorus, arsenic, and antimony. Incidentally some of the work on organic antimonials, at a later date, proved to be of interest to the Chemical Warfare Committee.

It is important to emphasise that Morgan's zeal for research never interfered with the conscientious discharge of a most congenial duty—the teaching of his students. Morgan enjoyed lecturing and took the greatest care in the preparation of his lectures. He spoke with easy, natural fluency, and the encyclopædic range of his knowledge in both inorganic and organic chemistry made his teaching both thorough and stimulating. He had a firm belief in the value of numerous and even elaborate lecture experiments. Nothing gave him greater pleasure than to see on his lecture table a display of beautiful specimens and to be able to illustrate his lecture by some particularly striking experiments.

During his association with the Royal College, Morgan was a very keen supporter of the Students' Chemical Society, at which senior students and others contributed scientific papers. He considered that participation in such activities was a most valuable part of the training of a chemist.

This important period in Morgan's career terminated in 1912 when he took up a Professorship in the Faculty of Applied Chemistry in the Royal College of Science for Ireland. He retained this appointment till 1915, and after a short time at British Dyestuffs Ltd. succeeded his former teacher, Meldola, as Professor of Chemistry at

Finsbury Technical College, where he remained till 1919. During the war years his publications were necessarily restricted, as he was engaged on work of national importance. His advice meanwhile was at the disposal of others, and those associated with him during the years of the Great War have recorded their gratitude to him for his ever-ready help and wise counsel.

In 1919 Morgan became Mason Professor of Chemistry in the University of Birmingham in succession to Professor P. F. Frankland, F.R.S. Morgan recalled with particular pleasure that his old teacher, Professor Sir William A. Tilden, had held the Chair of Chemistry in the Mason College, Birmingham, from 1880 to 1894 before he took up his Professorship at the Royal College of Science, London. The new professor entered on his duties with his usual enthusiasm and eagerly attacked the many problems confronting him. His first task was to re-equip the chemical laboratories. During the Great War the recently-built laboratories at Edgbaston had passed into the hands of the Army Medical Services and had been more or less devastated by their military occupants. In August, 1919, these modern laboratories again became available for University purposes, and thanks to the energy of the professor and his staff were ready to receive students at the beginning of the session. The University authorities at this time had adopted the bold policy of accepting ex-Service students from all parts of the country, with the result that every department was crowded with undergraduates far in excess of the annual entry of pre-war years. Morgan fully recognised that the duty of instructing these new students, many with meritorious war records, constituted a first call on the time and energies of the teaching staff. He did not forget, however, that "the true purpose of a University is to communicate to the minds of the young generation not only science in the state of completeness but also science in the state of growth", and to this end the provision of research facilities was vital. Research had always played an outstanding rôle in the activities of the Department of Chemistry at Birmingham, and Morgan determined that during his Directorship this tradition should be fully maintained. Although the teaching demands were heavy and engrossing, there was a spirit of renascence in the air, and very soon original investigations were proceeding in all the overcrowded laboratories, side by side with more elementary studies. The initiation of an active research school was made possible by two groups of research workers who had accompanied Morgan from Finsbury and constituted the nucleus of his research team.

One of these groups was maintained by the British Dyestuffs Corporation, the directorship of which at that time kept research colonies of chemists-in-training at University centres. These post-graduate students, who were engaged on the study of coal-tar intermediates and synthetic dyes, were valuable auxiliaries in the work of restoration of research activities. The other research group was made possible by the generosity of the Department of Scientific and Industrial Research, which had been formed during the Great War by the Government to make good the deplorable deficiency in our national facilities for fundamental investigations in pure and applied science. Out of this co-operation with the D.S.I.R. came the noteworthy researches on chelate co-ordination compounds carried out in collaboration with Dr. J. D. Main Smith, and the important investigations on organic derivatives of selenium and tellurium in which Morgan had the assistance of Dr. H. D. K. Drew. At this period Morgan devoted considerable attention to an experimental study of Werner's co-ordination theory of valency and chemical constitution.

In a comparatively short time Morgan had established a vigorous research school and he was enjoying to the full his teaching and his contacts with chemists in the Midland Area. He had gained in full measure the respect and affection of his staff by the confidence he freely reposed in them and by the freedom with which he invited and received their suggestions. Staff and students alike felt that to have worked with him was an experience to which they would always look back with gratitude. It was therefore with very mixed feelings that those associated with him at Birmingham learned that he had resigned his Chair in 1925 and had been appointed Superintendent of the new Chemical Research Laboratory of the Department o Scientific and Industrial Research. So began what Morgan himself described as a State experiment in Chemical Research and was destined to be the crown of his scientific career. He was admirably fitted for this important post by his manifold chemical interests, his great energy, and his ripe administrative experience.

The origin of the Chemical Research Laboratory is interesting. The work of the D.S.I.R. began in 1915, and during the next ten years the Department had become associated with certain chemical investigations which were carried out by groups of workers frequently located in widely separated laboratories. It was decided that some economy and increased efficiency could be realised by concentrating these research activities in a centralised laboratory. In furtherance

of this idea a suitable site was chosen on the Bushey Park Estate near the National Physical Laboratory, and in 1924 the building of the Chemical Research Laboratory began. The duty of advising the D.S.I.R. as to the programme of work to be undertaken was delegated to a Chemistry Research Board, which also exercised general supervision over its execution. At the outset executive control was vested in Sir Richard Threlfall, F.R.S., as a part-time Director of Research, and Morgan as whole-time Superintendent, but from 1927 onwards this responsibility devolved on Morgan as whole-time Director of Research. The fascinating story of this great venture was told by Morgan in the address he gave to the British Association at Bristol in 1930, when he was President of Section B. In this address he emphasised that a valuable function of the Chemical Research Laboratory is to provide competent and enterprising investigators with favourable opportunities for developing their inventive talent in work of national importance. That the laboratory fully discharged this function during Morgan's directorship is clear from the variety and range of researches which were undertaken. Investigations prosecuted with signal success included work on synthetic resins, low-temperature tar, high-pressure reactions, corrosion of metals, chemotherapy, and water-pollution. In addition, a limited amount of research in pure chemistry was always in progress, and here again the results obtained were of great value. No one privileged to pay a visit to this research centre will forget the obvious pleasure it gave to the Director to act as guide and to outline, with characteristic enthusiasm, the various researches which were in progress. Morgan was justly proud of the Chemical Research Laboratory, and visitors left it with a feeling of profound admiration for what had been achieved. When Morgan resigned his Chair at Birmingham to take up his new post at Teddington, certain doubts lingered in his mind as to the wisdom of his action. In later years he was fully convinced that his decision had been the right one, for he had been given unique opportunities of undertaking investigations which it would have been impossible to embark on in an academic post. No one could have been better fitted for the Directorship of the Research Laboratory at the particular stage of its growth, when it was winning the confidence of chemists and finding its way to public recognition. Now it is an established institution; then it was on its trial. As Director of the Research Laboratory, Morgan found full scope for his generosity of character, his optimism, his courage, and his resource. He carried

aloft a torch kindled from chemists of a great past. If others have kindled it from him and sustain it for the next generation, that service alone will entitle him to a high place amongst his contemporaries. When Morgan retired in 1938, this laboratory had won an important place amongst our national scientific institutions, and for this fine achievement Morgan was primarily responsible. He was too active to contemplate retirement, and he accepted an invitation to become Chairman of the Research Fund Committee of the Institute of Brewing. The Institute was very fortunate in securing his services. He entered upon his new duties with customary zeal and soon identified himself with this great industry by seeking the society of brewers, maltsters, hop-growers, and others interested in brewing research. His primary task was to determine the relative importance of the different branches of the Research Scheme of the Institute of Brewing, to assess the value of the work already done, and to mould future policy so that the maximum benefit might accrue to the brewing industry. His ideas on these matters were outlined in an address which was published in the *Journal* of the Institute of Brewing after his death, and one realises the valuable results which would have been obtained for the brewing industry if he had been spared to carry on his work.

Morgan brought many useful weapons to the battle of life—a singularly retentive memory, keen appreciation of the point at issue, considerable powers of organisation, and love of work. Yet to the many who knew him and admired him as a chemist and loved him as a man, the characteristic that was perhaps outstanding was his tireless energy. It was almost impossible to imagine Morgan as really idle. Above all, the impression always remains of an immensely industrious being who never spared himself. At the Royal College of Science after a day's teaching he would continue with his research work till the small hours of the morning, and at Birmingham and Teddington his working day was always a very long one. He was never bored or at a loss for an occupation and his well-stocked mind and phenomenal memory made his conversation stimulating and worthy of recollection. He was intensely interested in his fellow-men and much could be written of his clubbable qualities—his gift of friendship, his gaiety, his enjoyment of hospitality. A good companion indeed of whom every memory amongst his friends must always be happy and affectionate. Yet he was a reticent person. A trivial fact shows this. An old friend, on close terms of intimacy for many years, was never informed by Morgan of

his marriage. Amongst his finest attributes were his warmth of heart and ready sympathy. In a letter to *The Times* after his death a correspondent revealed that Morgan had made himself responsible for the cost of insulin treatment for one of his less fortunate neighbours at Essendon. Always the most approachable of men, he retained to the end that youthful gaiety of spirit which endeared him alike to young and old. He was always particularly happy in the company of young people. Many of his former students at Birmingham will recall with what regularity and keenness he attended the weekly dancing class held by his research and senior students. He was always deeply concerned for the welfare of his students, and had an almost parental solicitude for their future careers.

Any account of Morgan's life would be incomplete which does not emphasise his wit and humour. As a companion he was vivacious and ever ready to enjoy a good story. He could always see the humour of a situation, but his fun was never malicious. Lecturing on the Periodic Table he could not resist the temptation to tell his students to " think periodically ". A very talkative colleague who was proud of the fact that he had none of the common vices was dubbed by Morgan " an inert gas ". There is, however, no need to recall such things, for memories of his laughter, wit, and sense of comedy come quick and relentless. He was a " fellow of infinite jest ", and his friends will remember with affection his vivid personality.

Morgan was devoted to the Chemical Society and he served it well. He maintained that the Chemical Society merited the support of all members of the profession, for it had played the chief part in spreading chemical knowledge amongst British chemists and in securing general recognition for Chemistry throughout the Empire. He deplored the fact that much that the Society had accomplished in these directions had been under-valued by the rising generation, " who did not realise that with truly maternal instinct the mother-society had placed her resources freely at the disposal of the daughter societies ". Throughout his life Morgan was a regular attendant at the meetings of the Society, and he was particularly gratified if he could take part in some vigorous discussion after the reading of a scientific communication. For some years he was Editor of the *Journal*, and from 1910 to 1912 acted as an Honorary Secretary. On several occasions he served as a Vice-President and in 1933 he was elected President. His selection for the Presidency gave him great satisfaction, for he was proud to be included on the roll of

distinguished chemists who have held that high office. Other chemical organisations also claimed his interest. In the affairs of the Society of Chemical Industry he took a leading part and was a Past President. He received the Medal of the Society of Chemical Industry in 1939 and on this occasion delivered his address on "Personal Reminiscences of Chemical Research", which concluded with the passage: "This outline of experiments still in progress brings to a close my reminiscences of 50 years of chemical research. . . . It has been a most interesting and engrossing pursuit, not so very long when I now look backward, but rather like a watch in the night. There is still much to be done which I shall never do. But sooner or later a summation must be made and it now seems to me that my part in these enterprises has been mainly catalytic. At times I may have been able to direct such chemical investigations into specific channels, but on the whole much has been left to the goodwill and enterprise of many co-workers to whom I now desire to express my warmest gratitude and thanks."

Morgan's attachment to the Institute of Chemistry began in 1897 when he was elected to the Associateship, one of his examiners being Professor P. F. Frankland, F.R.S., his predecessor in the Chair at Birmingham. He became a Fellow in 1901 and later served as a Vice-President and as a Censor. Morgan took a very keen interest in the scheme for the award of National Certificates in Chemistry conducted under the Joint Committee of the Board of Education and the Institute of Chemistry. He acted as Chief Assessor from the inauguration of the scheme in 1921 until his death, and contributed greatly to its success. He was Chairman of the Bureau of Chemical and Physiological Abstracts, and during his tenure of that office devoted himself with great success to making these abstracts worthy of British Chemistry. It will be apparent that to few men was the cause of Chemistry nearer the heart than to Morgan. He was ever ready to take over responsible and arduous duties, and the spirit in which he worked is an inspiring example. An eminent statesman has said that there is only one form of congratulation in this world worth anything, and that is the expression of good will and the expression from your own peers that you have tried to do your duty. Morgan received this in full measure. As a member of the Council of the Chemical Society he was always ready to make his contribution to its proceedings, and he had very definite opinions on matters of policy. He cared passionately for causes, but it cannot be contended that he enjoyed the battle itself. Generally he was the patriotic

warrior prepared to go into battle when wanted, but at heart a lover of peace. Actually he was no politician but a bundle of generous enthusiasms.

Morgan gave much thought to the question of how our main chemical associations could effect economies in administration and provide a more comprehensive service of chemical publications. He considered that the co-operation of the three Chartered Bodies—the Chemical Society, the Society of Chemical Industry, and the Institute of Chemistry—if adopted, would represent only a very small advance. In Morgan's view it would be impossible for long to keep the scientific and professional aspects of chemical organisation in water-tight compartments, and he affirmed that already the lines of demarcation were becoming obliterated. His solution was a unified Society of Chemistry. However, he appreciated full well that the extent to which one all-embracing society could legislate for both the scientific and the professional needs of chemists was a knotty problem in any comprehensive scheme of reunion.

Over a period of some fifty years Morgan published alone or in collaboration 350 scientific communications. The subjects which he dealt with cover a very wide field, for he chose to disperse his interests rather than to concentrate them in one direction. It was a choice which gave him a scientific life full of variety and perhaps richer in pleasure than a more austere career could have been. Although he was fascinated by applied science, it never weakened his allegiance to pure science. He rightly maintained that applied science would fade and die unless the pursuit of knowledge was honoured in this country as the highest of human aims. To do full justice to the immense contributions which Morgan made to chemistry would require a much lengthier notice than is permissible here. Fortunately Morgan himself has dealt in detail with his chemical investigations in the address: "Personal Reminiscences of Chemical Research", which he delivered before the Society of Chemical Industry on July 11th, 1939. His selection of topics gives some idea of the range and importance of his researches. He discusses autoclaves, high-pressure reactions, chemotherapy, tar research, residual affinity and co-ordination, selenium and tellurium derivatives, non-aromatic diazonium salts, and a general reaction in diazo-chemistry. Although his contributions to these various chapters of chemistry are of definite significance, it is perhaps true to say that his name will always be specially associated with advances in the chemistry of co-ordination compounds. He had a profound admiration for the

genius of Alfred Werner, and this is readily discernible in the obituary notice which Morgan wrote for the *Journal* of the Chemical Society. Over many years, in the course of his investigations, Morgan accumulated a wealth of experimental data on co-ordination compounds. The particular value of those data was that they could be used to test the truth of the principles of valency and molecular constitution which were being laid down during the same period. As Sidgwick has very pertinently stated: "A theory of valency can only be justified by showing that it is applicable to chemistry as a whole: it is not enough that isolated examples can be quoted in its defence." Incidentally Morgan introduced the very convenient term "chelate", now so widely used for rings containing co-ordinated links. Amongst the problems which interested Werner was the close analogy between the lakes of mordant dyes and the metallic derivatives of β-diketones, and he expounded the view that mordant dyes were internal metallic complexes. After Werner's death, Morgan and Main-Smith began an examination of this idea and, selecting representative dyes, showed that any acidic substance capable of forming a colour lake must contain a chelate group capable of combining co-ordinatively with the metallic mordant. In every case examined the resulting lake proved to be an internal metallic complex. Morgan was always greatly intrigued by the chelate group acetylacetone, which enters into combination with the majority of metallic and metalloidal elements and even with certain non-metals. With H. W. Moss, he prepared and examined scandium acetylacetonate, and in collaboration with H. D. K. Drew isolated the acetylacetonates of gallium and germanium. Morgan was very fond of quoting a remark by Sir William Crookes, who, on hearing that scandium acetylacetonate could be distilled without decomposition under reduced pressure, declared that acetylacetone had "given wings to the metals". The contribution which Morgan made to the stereochemistry of co-ordination compounds is a very important one. With F. H. Burstall he resolved 6-covalent nickel, and thereby solved an outstanding problem. Again, his work with the polypyridyls as chelate groups has raised new stereochemical problems of great interest. Morgan was always fully alive to the contributions which physics could make to the solution of chemical problems. He was particularly interested in the application of *X*-ray methods to the solution of structural problems in both inorganic and organic chemistry.

In 1923 he published with Sir William Bragg a communication on

the structure of that curious compound, basic beryllium acetate, and was associated with Dr. Astbury in a paper on the structure and isotrimorphism of the tervalent metallic acetylacetonates. The so-called rarer elements had a definite fascination for Morgan, and he selected as the subject for his Presidential Address to the Chemical Society in 1935 his researches on the rarer elements. In this address Morgan described these researches, carried out in association with H. D. K. Drew, on organic derivatives of selenium and tellurium which resulted in the discovery of several entirely new groups of organo-metalloidal derivatives. One series of these tellurium compounds possessed exceptional germicidal properties in aqueous solution, but unfortunately they were somewhat poisonous and their bactericidal potency was greatly diminished in serum. Here it is worth recording that Morgan found the relationship between chemical structure and bactericidal activity a subject of particular fascination. Morgan's great interest in practical problems is reflected in this Presidential Address when he discusses the possibility of extracting germanium and gallium from Northumberland coal ash and describes a method for winning rhenium from Australian molybdenite.

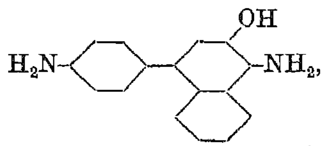
Throughout his life Morgan was irresistibly attracted by the chemistry of dyes. Few men had such an intimate knowledge of the history of the dyestuffs industry, and the revival of this industry in the post-war years gave him great satisfaction. He was a member of the Dyestuffs Licensing Committee and in that capacity rendered signal service to the industry. In 1921 he was awarded the Gold Medal of the Worshipful Company of Dyers, of which later he was a liveryman. Morgan joined the Company in 1923, and his seniority would have led to his election on the Court in the near future. To this he was looking forward not only because of his interest in the ancient Charter and Constitution, but also because the Company is very closely associated with the great dyestuffs and dyeing industries.

During a long life of service to chemistry many honours came to Morgan. He was elected F.R.S. in 1915 and received the Honorary Degrees of the Universities of Dublin, Birmingham, and St. Andrews. Amongst many other distinctions, he was a Fellow of the City and Guilds of London Institute, an Honorary Associate of the Manchester College of Technology, and an Honorary Member of the Society of Public Analysts. Morgan was an Associate Member of the Chemical Warfare Committee during 1914—18, and in January, 1920, was appointed an O.B.E. in recognition of his services. In 1936 he

received the honour of Knighthood for his services to science and the nation.

Sir Gilbert Morgan started life with few advantages except his natural abilities. It was his natural ability, his industry, and his courage which made him from an early period of life map out a scheme for his life's work. He was the architect of his own fortunes; he made his own friends, and he qualified himself for his career by ceaseless study from early years. His scientific interests were exceptionally wide, and he proceeded to make himself a master of every subject to which his keen mind was attracted. He was, it is true, exacting towards others, but he was not nearly so exacting towards others as he was towards himself. Morgan was one of that small but enviable band of men who compel other men to love them. And so to-day his friends think of him with wistful affection, as of one who has carried away with him some of their sunlight. He died as he would have desired, in harness, a harness put on himself in youth and worn triumphantly through a long life.

The Scientific Work of Gilbert Thomas Morgan.

Morgan's last Session at the Finsbury Technical College was spent in research work in the private laboratory of Professor R. Meldola. At that time Meldola and Streatfeild were occupied with their work on the diazoamino- and azo-compounds, and the subject of Morgan's first piece of research was closely related to this field: a study of the structure, then rather uncertain, of benzeneazo-β-naphthol and some of its analogues. In this Morgan was evidently successful, for he and Meldola published two papers as a result of his work of this single session (*J.*, 1889, **55**, 114, 603), in which is to be found some definite evidence in favour of the chemical constitution now current for the azo-compounds. Morgan prepared benzeneazo-β-naphthyl acetate and benzoate, and also the benzoate of *m*-nitrobenzeneazo-β-naphthol. By mild reduction of benzeneazo-β-naphthol and its acetyl and benzoyl derivatives, he obtained acetyl and benzoyl derivatives of the base 

, a diamine of the benzidine type, the structure of which he was able to recognise as the benzidine transformation was by then understood. He prepared also, with some difficulty, he tells us, the ethyl

ether of benzeneazo-β-naphthol, confirming an observation already made that alkylation of the azo-compound with alcoholic potash and an ethyl halide was never complete. In this case also a base of the benzidine type was isolated after reduction, and this was shown to be the diamine $\begin{array}{l} C_6H_4{\cdot}NH_2 \\ | \\ C_{10}H_5{<}\begin{array}{l}NH_2\\OC_2H_5\end{array} \end{array}$, by tetrazotising it and coupling with two molecular proportions of β-naphthol to give the violet tris-azo-compound $\begin{array}{l} C_6H_4{\cdot}N_2{\cdot}C_{10}H_6{\cdot}OH \\ | \\ C_{10}H_6{\cdot}N_2{\cdot}C_{10}H_5{<}\begin{array}{l}N_2{\cdot}C_{10}H_6{\cdot}OH\\O{\cdot}C_2H_5\end{array} \end{array}$. At that time, benzeneazo-β-naphthol was representable by the formula of Liebermann (I), by Zincke's hydrazone formula (II), or by the "old formula" (III), and only the last of these would give an *O*-alkyl derivative :

$$C_{10}H_6{<}\begin{array}{l}NH\\O\end{array}{>}N{\cdot}C_6H_5 \qquad C_{10}H_6{<}\begin{array}{l}N{\cdot}NH{\cdot}C_6H_5\\|\\O\end{array} \qquad C_{10}H_6{<}\begin{array}{l}N_2{\cdot}C_6H_5\\OH\end{array}$$

(I.) (II.) (III.)

Morgan found that the action of concentrated nitric acid on the ethyl ether of benzeneazo-β-naphthol reversed the original coupling by regenerating the diazonium salt, and at the same time caused nitration of the naphthalene ring; from this reaction product he isolated the ethyl ether of a dinitro-β-naphthol, $C_{10}H_5(NO_2)_2{\cdot}OEt$, melting at 138°. As this last substance must have been an oxygen ether, the reaction lent support to formula (III) for the unalkylated azo-compound.

Towards the end of 1889 Morgan entered the service of Messrs. Read Holliday, the Huddersfield firm of colour-makers, to whom he had been introduced by Meldola. In consequence, he did not again publish a scientific paper until 1898, although in the meantime he was continuously engaged in chemical investigations. He has himself given, in a lecture delivered in Exeter in July, 1939, a few details of his work at Huddersfield. He prepared, in the intervals of other work over a period of several years, the ten dihydroxynaphthalenes, afterwards making large-scale preparations of two of them : the 2 : 7-isomeride for use in the manufacture of the mordant *iso*nitroso dye, Gambine H, and the 1 : 5-isomeride, which was afterwards employed by others as an intermediate for Diamond Black PV, for use in what proved an unsuccessful search for a black vat dye.

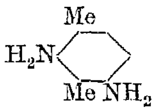
He took part also in the manufacture of a cotton dye, Titan Como Blue, now obsolete, produced by sulphonating tri-β-naphthyl-rosaniline; and he had charge of the large-scale preparation of *p*-nitroaniline, which was then replacing β-naphthylamine for producing ingrain dyes on cotton padded with β-naphthol.

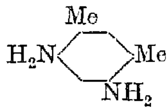
Morgan gave up his career as an industrial chemist in 1894, and resumed his scientific studies in London, this time at the Royal College of Science, where, after completing the course for the Associateship, he commenced research under Professor William Tilden. They first examined the bromination of pinene, with no very definite result; then, turning to a study of the carbohydrates of germinating wheat, they isolated the trisaccharide, raffinose, though they were anticipated in the publication of the discovery.

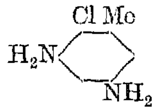
Soon afterwards Morgan joined the teaching staff of the College, where he remained until 1912. At first he resumed several researches suggested to him by his experiences with Messrs. Read Holliday, among which may be mentioned a study of the action of formaldehyde on naphthylamines, leading to naphthacridine derivatives (*J.*, 1898, 536; 1900, 814). From 1904 to 1912 much of Morgan's research work was performed in collaboration with a colleague, Miss F. M. G. Micklethwait, and a number of research students. Many of the topics were related to the chemistry of the diazonium reactions.

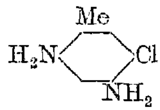
When an aromatic diazonium salt couples with an aromatic amine there is a possibility of the formation of a diazoamino- or of an azo-compound, but the outcome cannot always be predicted. Morgan began a lengthy study of this question in 1902, particularly in its relation to the *m*-diamines. At that time it was known from the work of Bernthsen, Bamberger, and others that the monoalkylated aromatic monoamines of the benzene series normally give mixtures of diazoamino- and aminoazo-compounds, whereas only the latter are given by the naphthylamines (including those containing hetero-nuclear substituents) and their monoalkylated derivatives, by diphenylamine, and by *m*-phenylenediamine and some of its homologues and substituted derivatives. Morgan found (*J.*, 1902, **81**, 86, 650) that of the two isomeric *m*-diamines (I and II) the first gave, with benzenediazonium chloride, a red azo-compound in high yield, whilst the second gave an unstable product from which only a small proportion of aminoazo-compound was obtainable. A second pair of isomeric *m*-diamines (III and IV) behaved in the same way, (III) resembling (I), and (IV) resembling (II); so that it was evident that

the essential feature of a *m*-diamine, in respect of the capacity to give a high yield of azo-compound, is the possession of an unsub-

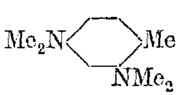

(I.)

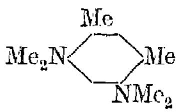

(II.)

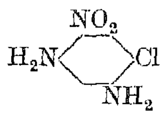

(III.)


(IV.)

stituted *para*-position to one of the amino-groups. It was shown, too, that the dialkylated *m*-diamines conform to this rule, since (V) gave a quantitative yield of azo-compound with *p*-nitrobenzene-diazonium chloride, whilst (VI) failed to react at all. Later,

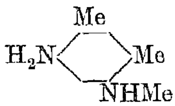

(V.)

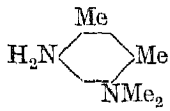

(VI.)


(VII.)

with W. O. Wootton (*J.*, 1905, 935), he examined the effect of a nitro-group as substituent in the *op*-position to the amino-groups: both (VII) and (VIII) gave good yields of azo-compound, although there is no unsubstituted *p*-position; and it was thus clear that the

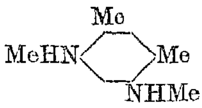

(VIII.)


(IX.)

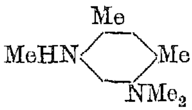

(X.)

influence of the strongly *m*-directive nitro-group was sufficient to promote coupling in the median position between the amino-groups. The mono- and di-methylated *m*-diamines were examined with Clayton and Micklethwait (*J.*, 1906, 1054; 1907, 360); of the examples tried, (IX) gave no diazoamino-compound and only a small yield of azo-compound; and the remaining three all gave diazoamino-compounds, with a fair proportion of azo-compound from (XI) but only traces from (X) and (XII). As all four diamines could only give rise to *o*-aminoazo-compounds, Morgan concluded that at least one of the amino-groups of the parent diamine must retain an aminic hydrogen atom in order that an *o*-azo-compound may be formed. Among β-naphthylamines, which usually give

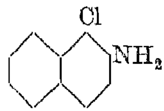
no diazoamido-compound, it was found that (XIII) is exceptional in this respect, resembling an already known exception (XIV);



(XI.)

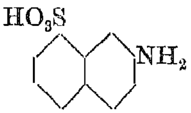


(XII.)

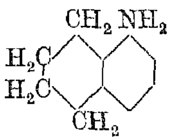


(XIII.)

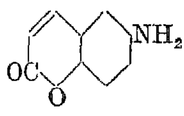
both these substances give diazoamines which are not changed into azo-compounds. The amines (XV) and (XVI), which bear a formal resemblance to the naphthylamines but have only one aromatic ring, were found also to give diazoamino-compounds (*J.*, 1904, 736, 1230).



(XIV.)

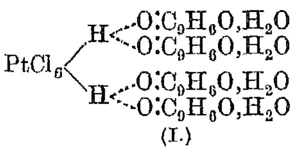


(XV.)

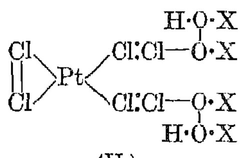


(XVI.)

The work on the coumarin derivatives had an important influence on Morgan's subsequent activities. With Miss Micklethwait, he noticed (*J.*, 1906, 863) that, when solutions of coumarin and platinic chloride in hydrochloric acid are mixed, yellow needles of coumarin platinichloride are obtained, of composition $4C_9H_6O_2,H_2PtCl_6,4H_2O$, and resolvable into its generators when treated with water. He recognised here an analogy with the γ-pyrone platinichloride of A. Werner (1902), of formula $4C_5H_4O_2,H_2PtCl_6$, to which Werner had assigned a structure on the basis of his theory of subsidiary valency. Coumarin platinichloride, according to Werner's theory, would then have had the structure (I); but at that time the co-



(I.)

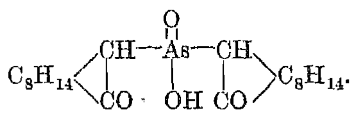


(II.)

ordination theory had not met with general assent, and Morgan preferred a structure (II) in which the higher valencies of oxygen and chlorine were invoked (X·O represents a coumarin molecule).

He did not long remain satisfied with this explanation, and a further study of the question convinced him of the justice of Werner's views; he became, in fact, one of the earliest admirers of the co-ordination theory, and never ceased to experiment upon its extensions.

Another topic to which Morgan adhered in the same manner was commenced in 1908: that of the organic derivatives of arsenic and antimony. The successful therapeutic application of "atoxyl" (sodium *p*-aminophenylarsonate) suggested to him a study of the interaction of arsenic acid and camphor. It was carried out with Miss Micklethwait (*J.*, 1908, 2144) by the condensation of sodium camphor and arsenious chloride in toluene, dicamphorylarsinic acid being obtained:

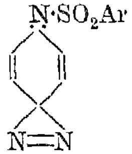


This was followed (*J.*, 1909, 1473; 1910, 34) by the preparation of tricamphorylarsinic acid, $(C_{10}H_{15}O)_3As(OH)_2$, and dicamphorylphosphinic acid, $(C_{10}H_{15}O)_2PO(OH)$, in collaboration with G. S. Whitby and W. R. Moore; work was aslo begun on triphenyl-arsine and-stibine derivatives, *e.g.*, $(NH_2{\cdot}C_6H_4)_3As{:}O$.

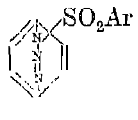
During the researches on antimonials, the orienting influence of antimonic substituents in the benzene nucleus was noted (*J.*, 1911, 2286): it was shown that the groupings $-SbO(OH)_2$, $=Sb(OH)O$, $\geqslant Sb(OH)_2$ were all preponderantly *m*-directive towards a group entering the benzene nucleus, the orientations being ascertained by replacing the antimonic group by a bromine atom through the action of phosphorus pentabromide, a known substance resulting. At that period little was known of the orienting effects of polar substituents of this kind: though Vorländer had discussed the matter as early as 1902, his main conclusions were given much later (1919).

In this period at the Royal College, Morgan began a long series of experiments *on the diazotisation of p-diamines containing a substituent in one of the amino-groups.* The work was pursued actively until 1913, and occasionally continued up to 1922. Some notable general conclusions were made. It was discovered (Morgan and Micklethwait, *J.*, 1905, 921, 1302) that the monoarylsulphonyl derivatives of *p*-phenylenediamine, when diazotised and the acidity of the reaction medium then diminished by adding sodium acetate

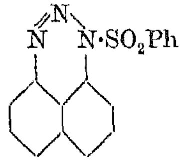
or by other means, gave sparingly soluble, yellow diazoimino-derivatives which could be reconverted into diazonium salts or coupled with phenols to form azo-compounds. The structures of the diazoimino-compounds, of which seven examples were given, could be represented by one or other of the alternative type formulæ (I) and (II) :



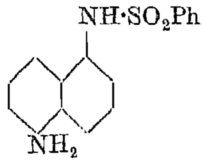
(I.)



(II.)



(III.)



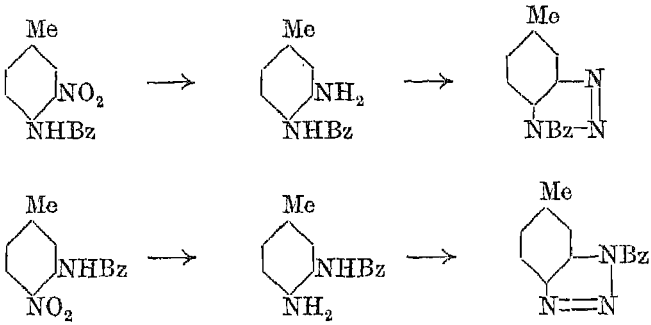
(IV.)

No reaction of this kind was then found when the acetyl, benzoyl, or succinyl group was employed in place of the arylsulphonyl; but shortly afterwards it was shown (*J.*, 1908, 602) that a picryl radical, $-C_6H_2(NO_2)_3$, can replace the arylsulphonyl group, and that if the nitro-groups of this radical are replaced one after another by hydrogen the diazoimines which result are progressively less stable. The degree of acidity of the grouping R in the diamine $H_2N\cdot C_6H_4\cdot NHR$ is therefore an important factor in diazoimine formation.

Long afterwards Morgan and W. H. Upton (*J.*, 1917, 187) discovered a method by which the simple acyl derivatives of *p*-phenylenediamine can be converted into diazoimines, although, as already mentioned, they fail to react under normal conditions. The method consisted in treating the acylated diamine with liquid nitrous anhydride (N_2O_3) in non-aqueous solvents, such as dry acetone.

The arylsulphonyl-*m*-diamines do not give diazoimino-compounds (*J.*, 1906, 1289; *Ber.*, 1906, 2869), as was to be expected from the behaviour of the unsubstituted *m*-diamines with nitrous acid. The unsubstituted and monosubstituted *o*-diamines, however, were known to react with nitrous acid, forming stable diazoimines which could not be smoothly converted into diazonium salts. In this latter group, Morgan had already shown (*J.*, 1906, 4), must be included 1 : 8-naphthylenediamine, which forms a diazoimide, and also its benzenesulphonyl derivative which gives a corresponding diazoimino-compound (III), whereas the anti-*peri*-isomeride (IV) gives none. Morgan and W. Godden (*J.*, 1913, 71) found that the two isomeric benzenesulphonyl derivatives of 1 : 2-naphthylenediamine gave rise to isomeric triazoles; similar pairs of these diazoimino-

derivatives were obtained (*J.*, 1913, 1391) from the acetyl and benzoyl derivatives of 3 : 4-tolylenediamine, *e.g.* :



The aminophenols present a somewhat similar case (*vide* Morgan and H. P. Tomlins, *J.*, 1917, 497), diazo-oxides being obtained from the *o*-, *p*-, and *peri*-compounds, but not from the *m*-; however, the diazo-oxides, even those derived from *o*-aminophenols, are able to regenerate the diazonium salts in presence of acids. When all these facts are taken together, it is still difficult to decide finally between type formulæ (I) and (II) for the *p*-diazoimines; in referring to the matter for the last time (1939) Morgan employed the quinonoid formula (I).

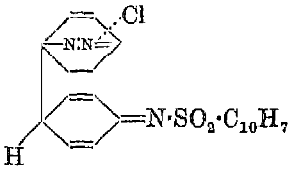
In connection with the diazoimines, Morgan's attention was drawn to the case of benzidine by a claim (D.R.-P. 51576) to the effect that on diazotisation under certain conditions this base was capable of yielding the internal diazoimide (I). With J. M. Hird (*J.*, 1907, 1505), he found that benzenesulphonylbenzidine gave rise

$$\begin{array}{ll} C_6H_4{\cdot}N_2 \\ | \qquad\;\; | \\ C_6H_4{\cdot}NH \end{array} \qquad\qquad \begin{array}{ll} C_6H_4{\cdot}N_2 \\ | \qquad\;\; | \\ C_6H_4{\cdot}N{\cdot}SO_2{\cdot}C_{10}H_7,2H_2O \end{array}$$

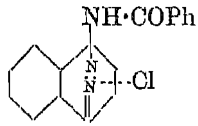
(I.) (II.)

to coloured diazonium salts which were apparently similar to a very stable, yellow diazonium chloride which he and Wootton had already prepared (*J.*, 1907, 1311) from benzoyl-1 : 4-naphthylenediamine. Under other conditions, however, it was later found (Morgan and Micklethwait, *J.*, 1908, 614) that a crystalline diazoimide can be produced from both the foregoing substance and naphthalene-β-sulphonylbenzidine, though both products had the unusual property

of retaining $2H_2O$ with extreme tenacity; replacement of the imino hydrogen of the initial sulphonylamino-group by an ethyl group inhibited the diazoimide formation. Morgan represented these diazoimides by formulæ as (II), perhaps in relation to Kaufler's hypothesis of the proximity of the amino-groups of benzidine (1907).



(III.)

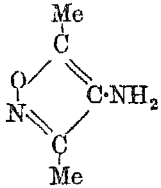


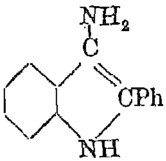
(IV.)

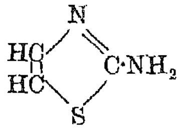
For the coloured diazonium salt, he mentions the tentative quinonoid formula (III); and, following a suggestion by Cain, he gives (IV) as the probable structure of the similar salt from benzoyl-1 : 4-naphthylenediamine. It is possible, in view of the subsequent supersession of Kaufler's theory, that formulæ (I) and (II) are to be regarded as polymeric.

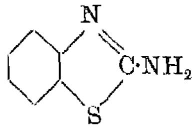
In 1912 Morgan went to Dublin as Professor of Applied Chemistry in the Royal College of Science for Ireland, a post which he held until 1915. There he began to study the application of the diazonium reactions to the semi-aromatic heterocyclic amines, preparing, with Dr. J. Reilly, Dr. C. V. Morrow, and J. W. Porter, a variety of diazonium salts from 4-amino-3 : 5-dimethylpyrazole, 2-aminothiazole, and some amino-triazoles (*J.*, 1913, 808; 1914, 435; 1915, 645, 1291). The first World War intervened, but Morgan afterwards resumed the work with Dr. H. Burgess in Birmingham (*J.*, 1921, 697, 1546). They prepared 3 : 5-*dimethylisooxazole from* acetylacetone and hydroxylamine, and succeeded in working out the conditions for its nitration and the reduction of the nitro-derivative to 4-amino-3 : 5-dimethyl*iso*oxazole (I), in substantial quantities; the rather difficult reduction was best achieved by means of aluminium amalgam in moist ether. Stable diazonium salts were isolated from the amine, and these gave rise to a number of highly coloured, crystalline azo- and other derivatives. Morgan suggests that those of the heterocyclic amines which are capable of being diazotised all contain the grouping $\gg C\cdot NH_2$, together with one other unsaturated centre giving $=C-C\cdot NH_2$ or $=C-N=C\cdot NH_2$, as is exemplified in the amino-derivatives of the pyridines, pyrroles,

pyrazoles, *iso*oxazoles, triazoles, indoles (as II), and thiazoles—including benzothiazoles—(as III and IV).


(I.)


(II.)


(III.)


(IV.)

During the war Morgan had returned to Finsbury Technical College as Professor of Chemistry. Here much of his energy was given to the chemical problems arising out of the war; but, with a few research assistants, he was able to carry on several investigations on azo-dyes and intermediates. With F. P. Evens, for example, a novel method was described (J., 1919, 1140) for the production in good yield of the not easily accessible β-naphthylmethylamine, by heating, at 200—220° under pressure, a mixture of β-naphthol and methylamine.

In 1919 he was appointed to the Mason Chair of Chemistry in the University of Birmingham, in succession to P. F. Frankland. He occupied this post during six years, with intense and restless activity. The researches which he conducted in this time were very varied in kind: the investigation of aromatic dyes and intermediates was continued and much work was devoted to the metallic derivatives of mordant azo-dyes and to other co-ordination compounds of the metals and to organo-metallic and -metalloidal compounds, particular attention being given to the structural and stereochemical aspects. Many of his publications, hovering between the inorganic and organic fields of chemistry, and impressed with his characteristic stamp, seemed to belong to an unusual hybrid branch, which J. F. Thorpe humorously proposed to call "Morganic chemistry".

In Dublin, Morgan had commenced, with H. W. Moss, a study of the metallic co-ordination compounds of acetylacetone, a β-diketone which is remarkable for its capacity to form compounds, of great variety of structure, with most metals and metalloids. They were able to prepare (*J.*, 1913, 78) an acetylacetone of tervalent vanadium (I), and to oxidize this, by means of moist air, to a vanadyl acetylacetone (II) containing quadrivalent vanadium. From a sample of scandia, the gift of Sir William Crookes, they obtained scandium acetylacetone, structure as (I), which proved to be volatile

under diminished pressure without decomposition (*J.*, 1914, 189).

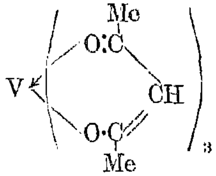
Scandium acetylacetone proved to be the analogue of yttrium acetylacetone in structure and general properties; and in 1927 Urbain and Sarkar found that ferric and scandium acetylacetones are isomorphous. On these relationships, Morgan has remarked: "Scandium may be regarded as the starting point of the first transition period of the elements, which includes iron, cobalt, nickel, copper, and zinc, and merges back into the normal series at gallium; and it is not surprising that scandium presents analogies with the transition elements as well as with the metals of the rare earths: $Na_3[Sc(SCN)_6],12H_2O$, and other similar thiocyanates of scandium, are isomorphous with the corresponding *iso*cyanates of the iron family; yttrium and lanthanum follow scandium as the starting points of the second and third transition series".

On his arrival at Birmingham University, Morgan resumed the work on the acetylacetones, and continued it for some years, extending it ultimately to a variety of other β-diketones with the assistance of a considerable number of research workers. He had received from Dr. J. H. Pollok about a decigram of metallic gallium prepared by its discoverer, Lecoq de Boisbaudran, and this was later supplemented by a gift of 2 grams of gallium hydroxide, of U.S.A. origin, from Professor C. James; with these, gallium acetylacetone, structure as (I), was prepared (*J.*, 1921, 1058), and compared with its already known aluminium and indium analogues; crystallographic examination, by T. V. Barker of Oxford, showed that gallium acetylacetone is dimorphous, its monoclinic form being isomorphous with aluminium acetylacetone, and its orthorhombic form with one of two orthorhombic forms of indium acetylacetone.

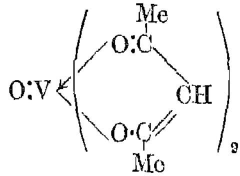
The acetylacetones of quadrivalent tin and germanium (*J.*, 1924, 372, 1261) proved more complicated: with tin, reaction ceases with the introduction of two β-diketone residues (*e.g.*, III), though, in presence of moisture, hydrated stanni-salts in which the central tin atom increases its co-ordination number from six to eight are formed (*e.g.*, IV); whilst with germanium analogues of type (III) are produced, but condensation also proceeds further to the stage shown in (V); the monohalogen derivatives of type (V) are able to combine with cupric halides to form intensely coloured germanium trisacetylacetone cuprihalides, which are unstable in organic solvents, producing the corresponding stable, colourless cuprohalides. With

A. R. Bowen (*J.*, 1924, 1252), Morgan showed that quadrivalent zirconium also forms complexes of type (V) with acetylacetone and other β-diketones, though zirconium tetra-acetylacetone can be produced in aqueous media.

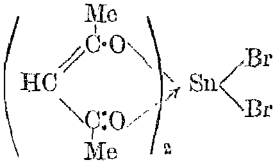
With the tetrachlorides of selenium and tellurium, however, it was found (*J.*, 1920, 1456) that acetylacetone behaves in quite another manner: co-ordination compounds are not produced, but in each



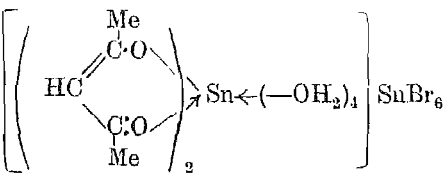
(I.)



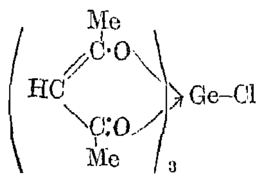
(II.)



(III.)



(IV.)



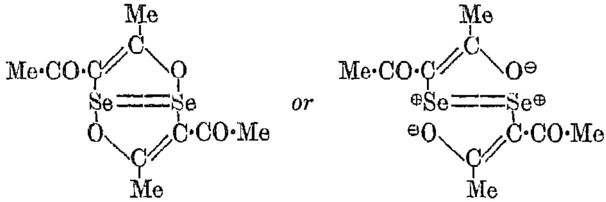
(V.)

case compounds are formed containing one metalloidal atom to one acetylacetone residue, this residue being derived by the subtraction of two hydrogen atoms from a molecule of acetylacetone; the selenium derivative (VI) is dimeric, whilst that of tellurium (VII) is not so but retains two of the original four chlorine atoms in union with tellurium (*J.*, 1922, 2432; 1924, 731, 1601). It was at first thought that the tellurium derivative had structure (VIII), but dioximes were later isolated, and it was found possible also to prepare an analogue (IX) from diethylacetylacetone, a non-enolisable β-diketone which could not possibly yield a derivative having the structure of type (VIII). With the help of Drs. C. R. Porter, H. G. Reeves, R. W. Thomason, and a number of others, Morgan extended the reaction with tellurium to a host of β-diketones, some of which contained aromatic groupings. It was found that a β-diketone of the general formula

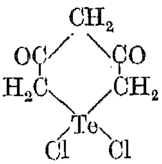
$$RH_2C{\cdot}CO{\cdot}CR''R'''{\cdot}CO{\cdot}CH_2R'$$

will yield a *cyclo*telluridichloride if R, R′, R″, R‴ are hydrogen or alkyl or arylalkyl (*e.g.*, benzyl) atoms or groups, and even if R″

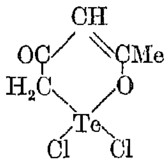
or R''' is a halogen atom, but that if any of the four remaining terminal hydrogen atoms of the above formula is replaced by any other atom or group, or if R, R', R'', or R''' is a purely aromatic group, such as phenyl, no cyclic tellurium compound results.



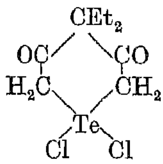
(VI.)



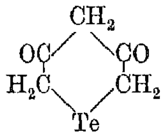
(VII.)



(VIII.)

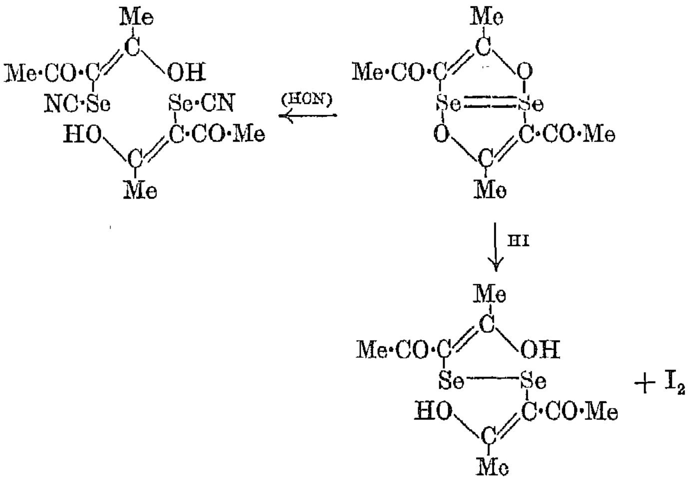


(IX.)



(X.)

The *cyclo*telluridichlorides are colourless and soluble only in organic solvents, but in all cases they are readily reduced by aqueous alkali bisulphites to *cyclo*telluropentanediones, as (X), which are crystalline



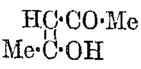
yellow substances, sublimable in a vacuum, and sometimes appreciably soluble in water. Morgan and E. A. Cooper (*Biochem. J.*,

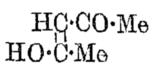
1924, 190, etc.) found that these substances have remarkable bactericidal properties *in vitro*, some of them ranking amongst the most powerful neutral agents known, in respect of certain organisms; but no use of them has yet been made, possibly owing to the toxic nature of bivalent tellurium.

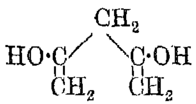
The condensation reaction between selenium tetrachloride and substituted β-diketones was likewise extended to benzoylacetone, dibenzoylmethane, and other β-diketones containing aromatic substituents. The structure of these selenium compounds was shown by opening the rings with hydrocyanic acid, hydriodic acid, and aromatic mercaptans, of which the scheme at bottom of p. 340 shows two examples. Selenium acetylacetone was found to be decomposed quantitatively with aqueous sulphurous acid or alkali bisulphite, giving selenodithionic acid, or one of its alkali salts, a reaction which is the most convenient method of making this inorganic acid :

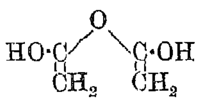
$$Se_2(C_5H_6O_2)_2+4H_2SO_3 = 2C_5H_8O_2 + 2Se(SO_3H)_2.$$

Summation of the foregoing studies of the metallic and metalloidal derivatives of acetylacetone led Morgan to the conclusion that the normal (aluminium, scandium, and other) acetylacetones of the metals are formed from the *cis*-modification (XI) of the middle-enolised form of the β-diketone, the *trans*-modification (XII) giving rise to the selenium derivative; with tellurium, on the other hand, the β-diketone reacts in a terminal-enolised form (XIII). This was an unexpected sequel; but a decisive test of the hypothesis was made


(XI.)


(XII.)


(XIII.)


(XIV.)

by carrying out the condensation with acetic anhydride in place of acetylacetone (*J.*, 1925, 531), thus eliminating altogether any possibility of middle-enolisation. The terminally enolised form of acetic anhydride would be (XIV), which should be able to react in the same way as (XIII). This expectation was in fact realised, the main products isolated being $Cl_2Te(CH_2{\cdot}CO_2H)_2$ and $Cl_3Te(CH_2{\cdot}CO_2H)$, readily derivable on a basis of the addition of $TeCl_4$ at the double bonds of formula (XIV). These substances, when reduced, gave, respectively, tellurodiacetic acid, (XV), and

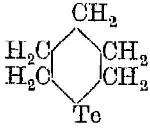
ditellurodiacetic acid, (XVI), the former of which occurs in a colourless and a yellow form, the latter being red.

$$Te{<}^{CH_2{\cdot}CO_2H}_{CH_2{\cdot}CO_2H} \qquad \begin{matrix} Te{-}CH_2{\cdot}CO_2H \\ | \\ Te{-}CH_2{\cdot}CO_2H \end{matrix} \qquad H_2C{<}^{TeCl_3}_{TeCl_3} \qquad H_2C{<}\begin{matrix} Te \\ | \\ Te \end{matrix}$$

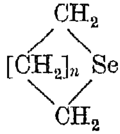
(XV.) (XVI.) (XVII.) (XVIII.)

A by-product of unusual character was the crystalline methylenebistelluritrichloride (XVII), which on reduction gave the red cyclic substance, ditelluromethane (XVIII), or a polymeric form of that structure, containing over 94 per cent. of tellurium; the freshly filtered substance changed to a black form when touched, but it retained its structure—since it was readily reconverted to (XVII) by the action of chlorine; ditelluromethane explodes with a green flash when gradually heated.

Morgan afterwards continued the experiments with selenium and tellurium at the Chemical Research Laboratory, Teddington, in conjunction with Dr. H. Burgess and F. H. Burstall. The parent of the already mentioned cyclic tellurium compounds, *viz*, *cyclo*telluropentane (XIX), was synthesised through the interaction of aluminium telluride and ωω′-pentamethylene dihalide (*J.*, 1928, 321), and subsequently the smaller-ring compounds, *cyclo*telluro-propane and -butane were obtained. The selenium analogues of these cyclic compounds were similarly prepared by Morgan and Burstall (*J.*, 1929, 1096, 2197; 1930, 1497) from sodium selenide and polymethylene dihalides; and they extended the range of the reaction to prepare a truly remarkable series of selenohydrocarbons, with rings containing from 3 to 18 methylene groups (general formula XX).



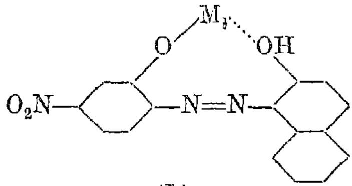
(XIX.)



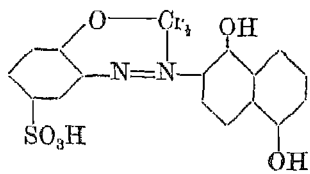
(XX.)

During the Birmingham period, Morgan also undertook an extensive examination of the cobalt and chromium lakes of the mordant dyes with a view to determining their structure and thus throwing light on the mordanting processes used in the dyeing industry. He had previously begun this subject with Porter and Evens in the period 1915—19, and he now collaborated with Dr. J. D. Main Smith, Dr. King, J. E. Moss, and others in researches on the lakes formed by nitrosonaphthols, alizarins, salicylic acid, and

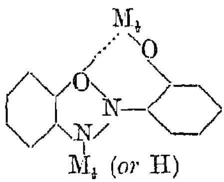
mordant azo-dyes, using chiefly the metals cobalt, chromium, and iron (*J.*, 1921, 704; 1922, 160, 1723, 1956, 2857, 2866; 1923, 1096; 1924, 1329; *J. Soc. Dyers and Col.*, 1925, 233). A large number of highly complex, co-ordinated lakes, many of them containing also ammonia molecules in attachment to the metal atoms, were prepared and analysed. Initially, Morgan had adopted the structure suggested by Baudisch for the lakes of tervalent metals in combination with *o,o'*-dihydroxyazo-dyes, as, for example, in (I), where the dotted bond expresses a supplementary valency linking; but as a result of the work at Birmingham he afterwards modified this view by assuming that the second *o*-hydroxyl took no part in the inner lake formation with the dye, the co-ordination link being supplied by one of the nitrogen atoms of the azo-group, as in (II), which shows this view of the chromic lake of Diamond Black PV in its simplest form. In this structure, as given below, the exposed sulphonic acid and



(I.)



(II.)

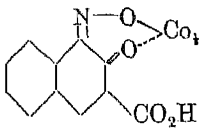


(III.)

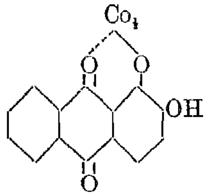
hydroxyl groups are shown free; but in most of the actual lakes isolated by Morgan and his collaborators such groupings were combined in simple salt formation with further metallic atoms which were sometimes co-ordinated with ammonia or water molecules. This simple salt formation, however, is immaterial to the structure of the true inner lake, and is omitted in this memoir. Structures such as (II) suggested that the *o*-monohydroxyazo-dyes, also, should yield inner lakes; but, as no evidence of such could be obtained on making trials, Morgan ultimately suggested two alternative views: either, that the function of the second *o*-hydroxyl group was to increase the lake-forming power of the first hydroxyl;

or else, that an amended type of formula (as III) should be employed to express the lakes.

Morgan confirmed types of structures which had already been postulated for the lakes of the quinone oxime and alizarin classes of dyes: the essential form of the inner lakes was found to be as shown in the two examples, (IV) and (V), any free hydroxyl, carboxyl, or other similar groups being usually combined in simple salt formation with further metal.



(IV.)



(V.)

Morgan's papers on the lakes of the azo-dyes containing two *o*-hydroxyl groups, or sometimes one *o*-hydroxyl and an *o′*-amino-group, constituted the earliest published detailed work on this theoretically and industrially important problem; and, although it is not so far known that any of the lakes of this class which he described is actually produced when fibres are dyed and mordanted or directly dyed with metallised dyes, his work brought into view some of the essential features of lake formation at a time when very little precise information on the subject was available.

Among the many miscellaneous researches made at this time, the following contain points of special interest. With G. R. Davies (*J.*, 1923, 228), it was found that, although two-fold diazotisation of nitrodiaminomesitylene could be performed in one operation and the product could be coupled with two molecular proportions of resorcinol, nevertheless triaminomesitylene could not be caused to undergo threefold diazotisation; if two of the three amino-groups were diazotised and replaced by azo-groupings (by coupling with a phenol) or by azide groups, the remaining amino-group could then be diazotised and replaced or coupled: it was concluded that a single benzene nucleus cannot carry more than two diazonium groups at a time. Morgan prepared, with Dr. S. R. Carter and A. E. Duck (*J.*, 1925, 1252), the compact nonane, tetraethylmethane, and compared its properties with those of the known tetraethyl derivatives of silicon, germanium, tin, and lead. With O. C. Elvins (*J.*, 1925, 2625), it was found that tellurium tetra-

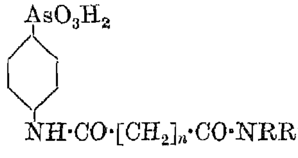
chloride could be condensed with the simple aliphatic ketones, one or two ketonic residues replacing chlorine atoms; thus, acetone gave $Cl_2Te(CH_2{\cdot}CO{\cdot}CH_3)_2$, and methyl ethyl ketone gave $Cl_3Te(CH_2{\cdot}CO{\cdot}C_2H_3)$, whilst pinacolin gave a separable mixture of both kinds of derivative; these reactions, like those with the β-diketones, are compatible with the hypothesis that the enolised forms of the ketones react. A re-examination of that curious and seemingly inexplicable substance, basic beryllium acetate, was carried out in 1923, with C. R. Porter, in conjunction with Sir William Bragg and Dr. W. T. Astbury; the substance has the formula $Be_4O(CH_3{\cdot}CO_2)_6$ and is completely non-ionised, being insoluble in water but crystallisable from organic solvents; the *X*-ray examination showed that the four beryllium atoms are at the vertices of a tetrahedron, with the unique oxygen atom at the centre and each of the six acetate groups spanning an edge of the tetrahedron. With Drs. W. J. Hickinbottom and T. V. Barker (*Proc. Roy. Soc.*, 1926, 502) a base containing two structurally similar asymmetric carbon atoms, *viz.*, βγ-di-*p*-tolylamino-*n*-butane, was prepared in four distinct, crystalline forms corresponding with the four forms of tartaric acid completed by Pasteur.

Morgan left Birmingham in 1925, on his appointment as Superintendent of the new Chemical Research Laboratory of the Department of Scientific and Industrial Research, at Teddington, Middlesex. It was only after two nights of great mental stress, he has averred, that he was able to decide to part finally from academic chemistry; but he was afterwards satisfied that he had come to the right decision.

The Chemical Research Laboratory rapidly expanded into a great experimental station dealing with research problems in many branches of chemistry, both inorganic and organic. In 1932, some six years after its opening, the Laboratory was carrying out investigations on the following major topics, among many others: the identification and separation of the constituents of low-temperature coal tar and aqueous tar liquors; high pressure catalysis of carbon monoxide–hydrogen mixtures; the extraction of helium from monazite sand; the catalytic hydrogenation of phenols and resinous constituents of coal tar; the derivation of synthetic resins from coal tar products; the amination of organic compounds under high pressures. Such activities must have been the concern of many minds, but certain other researches of a more academic character were carried out under Morgan's personal supervision and are

described in the scientific journals. Some of the topics are mentioned below.

In conjunction with Dr. E. Walton and others, Morgan continued the work on the therapeutic properties of the organic compounds of arsenic, particularly the derivatives of *p*-arsanilic acid of the series indicated in the type formula :



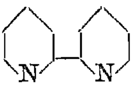
Representative members were prepared through the series from $n = 0$ (oxanilic), in the above formula, to $n = 16$ (hexadecanedicarboxylanilic); and many of them were examined for toxicity and for trypanocidal activity (*vide*, *e.g.*, *J.*, 1933, 91 ; 1938, 442). Morgan has mentioned especially the sodium salt of the methylamide of *p*-arsonophenylsuccinamic acid, which, under the name of "neocryl", was on trial in the treatment of sleeping sickness (1939) :

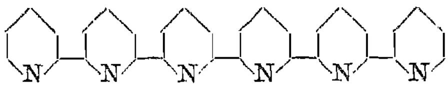
$$Na(H)O_3As{\cdot}C_6H_4{\cdot}NH{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}CO{\cdot}NH{\cdot}CH_3.$$

Here it may be mentioned that Morgan published, in 1918, a volume in the series of Monographs on Industrial Chemistry entitled "The Organic Compounds of Arsenic and Antimony".

During the years 1931—38, Morgan and F. H. Burstall carried out at Teddington a study of the preparation of polypyridyls and of the structure of their co-ordination compounds with the metals. The bromination of pyridine in the vapour phase, in the presence of a catalyst, usually gives 3-bromo- and 3 : 5-dibromo-pyridine at 300° ; but at 500°, or at 300° in the presence of ferrous or cuprous bromide, it gives good yields of 2-bromo- and 2 : 6-dibromo-pyridine, the bromine in which is readily replaceable by other groups. Removal of the bromine of 2-bromopyridine with copper bronze leads to 2 : 2-dipyridyl, (I). Morgan and Burstall found (*J.*, 1932, 20; 1934, 1498) that this substance could also be prepared by the dehydrogenation of pyridine with anhydrous ferric chloride or other metallic chloride. Burstall later showed that a series of α-polypyridyls can be prepared by repeated bromination and condensation with copper powder in boiling diphenyl, or by further dehydrogenation of lower α-polypyridyls with ferric chloride (*J.*, 1938, 1662).

In this manner all the α-polypyridyls up to α-hexapyridyl, (II), were obtained.


(I.)


(II.)

Morgan made use of these polypyridyls as polydentate groups which were able to co-ordinate with metallic atoms through the *residual affinities of the conveniently aligned nitrogen atoms.*

With the use of α-dipyridyl, optically active complexes of bivalent nickel were obtained for the first time (*J.*, 1931, 2213). The method employed was to prepare [Ni 3dipy]Cl_2 from α-dipyridyl and nickelous chloride and then to treat this with ammonium *d*-tartrate; the resulting *d*-trisdipyridyl nickelous *d*-tartrate gave the corresponding *d*-chloride on double decomposition with ammonium chloride; by the use of the *l*-tartrate, the enantiomorphic *l*-chloride was obtained. The optical activity of these complexes is due to the octahedral arrangement of the three chelate dipyridyl groupings about the nickel atom, and it is of interest that the active complexes were found to racemise readily in aqueous solution and even when kept as crystals. The corresponding ferrous bromide and iodide complexes had already been resolved by Werner, and later on Burstall resolved a similar salt of bivalent ruthenium, [Ru 3dipy]Cl_2.

Morgan and Burstall had been led to the discovery of α-tripyridyl from the intense purple colour which it produces in presence of ferrous salts, a reaction which provides a specific test for ferrous ions up to a dilution of 1 part in about 2 million parts of water. They now isolated the complex bromide, [Fe 2tripy]Br_2, containing the kation responsible for the colour, and they prepared analogous complex salts of bivalent chromium, cobalt, nickel, ruthenium, and osmium; all of these they regarded as possessing octahedral symmetry, though they pointed out that there are three possible ways of arranging two tridentate groups around the octahedron.

Bivalent zinc, cadmium, and mercury, and also univalent silver, gave complexes with only one tripyridyl group associated with each atom of metal, and these derivatives may be polymeric. Complexes of bivalent silver were obtained also with one tripyridyl group per atom of silver; these were regarded as monomeric compounds of planar form, as also were analogous derivatives of bivalent palladium and platinum; on the other hand, tervalent iridium and quadrivalent platinum gave 6-co-ordinated, octahedral complexes,

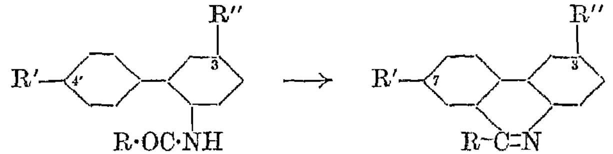
[tripy Ir Cl_3] and [tripy Pt Cl_3]Cl (*J.*, 1937, 1649; cf. *J.*, 1934, 1498).

The co-ordination of metals with α-tetrapyridyl was also examined (*J.*, 1938, 1672). The case is of exceptional interest, since the tetrapyridyl contains four possible co-ordinating centres and there may be free rotation of the rings with respect to one another. It was found that univalent silver and bivalent zinc, cadmium, iron, cobalt, nickel, copper, and platinum all yield 4-covalent complexes containing the kation [Me tetrpy], where Me represents an atom of the metal; but tervalent cobalt and iridium give complexes having the kation [$MeCl_2$tetrpy]. Morgan suggested that probably the 4-covalent derivatives of iron, zinc, and cadmium have a planar configuration, as was at that date already recognised for the 4-covalent derivatives of copper, silver, manganese, cobalt, nickel, platinum, and palladium. The quadridentate group of the complexes of the tervalent metals still had a planar disposition, the two chlorine atoms completing an octahedron by assuming *trans*-positions. His last papers on this subject describe, respectively, the isolation of complexes of quadrivalent ruthenium in association with a polypyridyl and a nitroso group (Morgan and Burstall, *J.*, 1938, 1676), and the isolation of rhenium from Australian molybdenite (Morgan and Davies, *J.*, 1938, 1861) by final separation as the colourless tripyridyl per-rhenate, $(C_{15}H_{11}N_3H)ReO_4$, or as dipyridyl per-rhenate—which is more soluble in water than the molybdenum analogue.

While the Laboratory at Teddington was being built, Morgan had again taken up the experiments on the phenol–formaldehyde condensations. With A. A. Drummond, N. J. L. Megson, and E. L. Holmes, the reactions with *m*-cresol and higher phenols were examined, and it was noticed that acetone was a favourable medium for the production of resins. This led to the study of the condensation of simple aliphatic ketones with formaldehyde and to the preparation of transparent resins from acetone and from methyl ethyl ketone. By 1939, with the help of further improvements made by Drs. Griffith and Pepper, a transparent and colourless resin had been produced from the latter ketone and formaldehyde. Morgan described the properties of this resin as promising, and he attributed its formation to the polymerisation of $Me{\cdot}CO{\cdot}CMe{:}CH_2$, derived by simple dehydration of the initial condensation product, $Me{\cdot}CO{\cdot}CHMe{\cdot}CH_2{\cdot}OH$.

A few alkaloids, such as lycorine and tazettine, are known to be

based on the phenanthridine structure. Morgan became interested in the phenanthridine series as possible agents against bacteria and trypanosomes. With Dr. L. P. Walls, he found a favourable variation of the known process of ring closure of the *N*-acyl derivatives of *o*-aminodiphenyl to give phenanthridines, by employing phosphorus oxychloride as the condensing agent. The older process of Pictet and Hubert made use of zinc chloride, and it had the disadvantage that it could not be applied to derivatives containing nitro- and other reactive groupings; the yields, also, were poor.

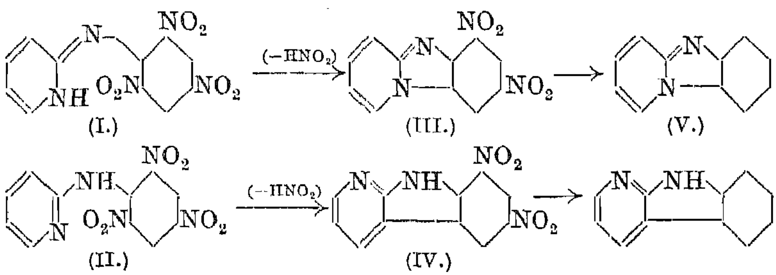


With phosphorus oxychloride, it was possible to prepare a variety of substituted phenanthridines containing alkyl, chloroalkyl, phenyl, and nitrophenyl substituents (*J.*, 1931, 2447; 1932, 2225; *vide* also *J.*, 1938, 389). It was noticed that when R = Me in the above reaction scheme and at the same time R′ = NO_2 and R″ = H or NO_2, there is a side reaction producing resinification and a much diminished yield of the phenanthridine. In these cases, replacement of the methyl group, R, by a phenyl or a *p*-nitrophenyl group allows smooth, though slow, ring closure to occur. If R′ = H, however, there is smooth ring closure when R″ = NO_2, even if R = Me; in fact, the presence of a nitro-group in position 3 favours, but in position 4′ hinders, the ring closure. A number of phenanthridinium salts were prepared from the phenanthridines, some of which possessed trypanocidal activity.

An immense amount of research had been carried out on the catalysis of the reactions which occur between carbon monoxide and hydrogen at high pressures, of which methanol is the most important product. Morgan, however, by introducing modifications in the catalyst, was able to show that a number of fresh substances could be produced under certain conditions in this reaction. In particular, it was shown (Morgan and R. Taylor, *Proc. Roy. Soc.*, 1931, *A*, **131**, 533) that ethyl alcohol could be produced in considerable proportion, whereas previously only traces had been observed in such reactions. A granular catalyst, made from cobalt nitrate and commercial zinc permanganate, incorporated, after roasting, with potter's clay, and finally reduced in hydrogen, was used, with a mixture of two volumes

of hydrogen and one of carbon monoxide circulating at 200 atmospheres, the catalyst being heated at 380—410°. The main products were methane and a mixture of alcohols, of which ethyl alcohol was the principal constituent; thus, of the total products of reaction, some 10% of the carbon was present in ethyl alcohol and some 2% in acetaldehyde. Potash, to the amount of some 7—8%, was present in the catalyst referred to above; and it was afterwards found (Morgan, D. V. N. Hardy, and R. A. Procter, *J. Soc. Chem. Ind.*, 1932, 1T) that a catalyst of chromium and manganese oxides impregnated with an alkali hydroxide, the best being rubidia for this purpose, led to the production chiefly of methanol and a mixture (in about the same proportion) of higher alcohols, aldehydes, and acetals; among these, ethyl, propyl, butyl, *iso*butyl, *n*-amyl alcohols, and 2-methylbutanol, were identified.

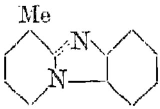
In preparing some new bases of the pyridine series, for examination as colour intermediates or therapeutic agents, Morgan and Dr. Jessie Stewart discovered a notable condensation reaction leading, through ring closure, to cyclic 1 : 3-diazalines. They had prepared 2-amino-*N*-2′ : 4′ : 6′-trinitrophenylpyridine by condensing 2-aminopyridine with picryl chloride in benzene solution at the boiling point; but when the preparation was carried out in toluene solution, nitrous fumes were evolved and the product was a mixture of 2-aminopyridine hydrochloride and a yellow substance of very high melting point. The yellow substance was found to be practically the sole product when dimethylaniline was used as the solvent, or, simply, when 2-aminopicrylpyridine was slowly heated to its melting point. It was identified as the cyclic 1 : 3-diazaline, 4 : 6-dinitropyrido(1′ : 2′ : 1 : 2)benziminazole, (III), the formation of which can be represented as an inner condensation of one of the two possible tautomeric forms, *viz.* (I), of the *N*-substituted 2-aminopyridine :



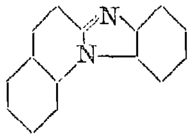
(I.) (III.) (V.)

(II.) (IV.)

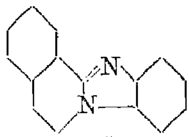
The other tautomeric form should give dinitro-α-carboline (IV); but reduction of the two nitro-groups of the product, followed by replacement of the resulting amino-groups by hydrogen atoms, gave rise, not to α-carboline, but to an isomeric, colourless base, which must therefore have been (V). The general applicability of this condensation reaction was demonstrated by preparing in the same manner the respective *1 : 3-diazalines (VI—IX) from the 2-amino-* derivatives of β-picoline, quinoline, *iso*quinoline, and phenanthridine :



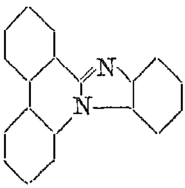
(VI.)



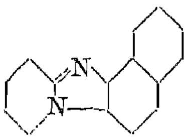
(VII.)



(VIII.)



(IX.)



(X.)

In a later *publication (J., 1939, 1057) the scope of the reaction* was further extended by showing that 1-chloro-2 : 4-dinitro-benzene and -naphthalene can be substituted for picryl chloride in the 1 : 3-diazaline synthesis; for example, the use of the naphthalene derivative leads eventually to (X), through its 7-nitro- and 7-amino-derivatives, the base used initially being 2-aminopyridine.

The paper just mentioned was the last of Morgan's scientific publications. It was received in April, 1939, when he had completed the fiftieth year of his association with chemical research. In July of the same year he gave in a lecture a brief account of his experience : " It has been a most interesting and engrossing pursuit ", he said in concluding, " not so very long when I now look backward, but rather like a watch in the night." He died at Richmond on February 1st, 1940.

Morgan was interested, almost equally, in all branches of chemistry. His work, scattered, in consequence, over a great many subjects of inquiry, yet never failing to bring new knowledge, has rather diffused an illumination over the science as a whole than singled out any of

its particular aspects. The prominence which he gave to the theory of co-ordination, at a time when it received little recognition in many lands, was an important influence in its rapid development and manifold application. Of equal, or perhaps greater value were his numerous researches in aromatic chemistry, providing a great body of information on chemical behaviour and supplying many new methods and substances which have found application in technology. He was in fact both an academic and an industrial chemist: the character of his work, as well as his attitude, served as a link between the two groups, by showing that their aims and methods, when both are at their best, are almost identical. "Much remains to be done which I shall never do" he had said near the close, but much, surely, he had accomplished.

[Photo: Lafayette, Ltd.

ARTHUR LAPWORTH

ARTHUR LAPWORTH

1872—1941

ARTHUR LAPWORTH was born on October 10th, 1872, at Galashiels; his father was Charles Lapworth (F.R.S., 1888, Royal Medallist, 1891), the eminent first Professor of Geology in the University of Birmingham, who was a pioneer in laying the foundations of stratigraphy. After early education at St. Andrews and at King Edward's School, Birmingham, he graduated at Mason College and, as an 1851 Exhibitioner (1893—95), proceeded to the City and Guilds of London Institute, where the presiding genius was H. E. Armstrong. However, Lapworth came more directly under the care of F. S. Kipping, who was at that time in charge of the main organic laboratory.

Professor Kipping writes :

"From the very first it was obvious that Lapworth had the experimental skill, as well as the powers of acute observation and sound deduction which would ensure his success in scientific work, and that his vivid imagination and high intellect would take him far in his profession. Any one who made Lapworth's acquaintance could not fail to wish for closer ties, and although he was considerably my junior in age we soon became fast friends; perhaps it would be truer to say that our relationship, even in those early days, was rather that of congenial brothers. He became a frequent visitor at our house in South Kensington, where he often met Pope, Forster, and other workers in Armstrong's laboratories, and my wife soon shared with me the great pleasure of his friendship. During one vacation when he had made no holiday plans, we asked him to stay with us at Bridgwater : here it was that he met his future wife, Kathleen Holland, with whom during forty years he spent the rest of his life in peaceful and loving marital harmony."

To this may be added that Kathleen was the younger sister of Mrs. Kipping and of Mrs. W. H. Perkin, thus Mrs. Holland was the mother-in-law of three distinguished chemists and Fellows of the Royal Society.

His postgraduate course at the "Central" included crystallography under the late Sir Henry Miers and following this he worked with Armstrong on the sulphonation of ethers of β-naphthol and with Kipping on derivatives of camphor and camphene. So began two of his main interests in later research, the chemistry of camphor and the mechanism of aromatic substitution. His D.Sc. thesis,* submitted at the age of twenty-three, on the naphthalene topic was the occasion for a characteristic display of courageous independence. He refused to alter some sections of the theoretical treatment which his formidable professor had criticised.

Lapworth's first post (1895) was that of Demonstrator in Collie's laboratory at the School of Pharmacy in Bloomsbury. One joint paper (*J.*, 1897, **71**, 838) on picoline derivatives from this period bears the Collie stamp. In 1900 he went to the Goldsmiths' Company's Institute at New Cross as Head of the Chemistry Department (1906, Goldsmiths' College) and in 1909 became Senior Lecturer in Inorganic and Physical Chemistry and Schunck Fellow at the University of Manchester. Four years later he succeeded W. H. Perkin, jun., in the Chair of Organic Chemistry and in 1922 became Sir Samuel Hall Professor (primarily responsible for physical and inorganic chemistry) and Director of the Laboratories. The writer, first as a Junior Demonstrator and, after an interval of years, as Professor of Organic Chemistry, had the inestimable privilege of his friendship and collaboration. At lunch in the refectory and at many other times we exchanged ideas, often expressed on the back of envelopes by what Armstrong was pleased to call "noughts and crosses". During this latter period Mrs. Lapworth acted as his secretary in the department.

His last appointment demonstrates Lapworth's remarkable breadth and versatility; very few men in the twentieth century would be thought competent to hold in succession chairs of organic and physical chemistry. He retired in 1935 and was appointed Professor Emeritus. He was elected F.R.S. in 1910, served on the Council (1927—29), received the Davy Medal in 1931, and was an honorary LL.D. of Birmingham and of St. Andrews universities. These distinctions are mentioned with some uneasiness; high as they are they afford no measure of the achievement of a man whose influence on chemical philosophy was outstanding.

His modest disposition did not bring him into the limelight; he

* "Sulphonic acids of betamethoxy- and betaethoxy-naphthalene." Thesis for D.Sc. (London), April, 1895.

was not a showman, tending rather to disparage his wares; he made no dramatic discoveries such as to catch the public eye; he never flogged a dead horse and even left some promising live ones to fend for themselves. He investigated in order to learn something, to educate himself, and not with the primary object of producing elegant and finished scientific memoirs, though he did indeed leave many such on record. Much of his work seems, therefore, incomplete, and his output of over a hundred papers was, judged by some standards, relatively small. Yet the power of his genius triumphed and it is now possible to see how his ideas, always many years ahead of those of his contemporaries, played a leading part in the contribution which organic chemists have made to the revolution in chemical thought. The electronic theory of valency has made it possible to give a measure of precision to many of the suggestions he advanced on an electrochemical basis, but Lapworth's preparation of the ground was essential. During many years little attention was paid to his views; now they are the commonplaces of the textbooks.

One of Lapworth's first major interests was the constitution of camphor and the way he attacked the problem was very significant. There are quite a number of ordinary papers on the detailed chemistry of derivatives; just the kind of thing that many workers in the field could, and did, produce. Certainly some of this material was of great importance and demonstrated his skill as an experimentalist, in particular his study of homocamphoric acid (*J.*, 1899, **75**, 986; 1900, **77**, 446, 1053) forged a vital link in the chain of evidence. In this investigation he showed that homocamphoric acid can be degraded to dehydrohomocamphoric acid and then to camphononic acid, which must be a *cyclo*pentane derivative because it could be synthesised by ketonisation of homocamphoronic acid.

$$C_7H_{13}\begin{cases} CO_2H \\ >CH\cdot CH_2\cdot CO_2H \end{cases} \qquad\qquad C_7H_{13}\begin{cases} CO\diagdown \\ \quad\; >CH_2 \\ >CH\diagup \end{cases}$$

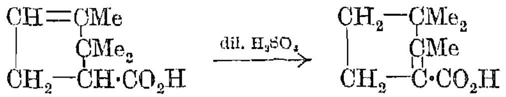
Homocamphoric Acid *Camphor*

$$C_7H_{13}\begin{cases} CO_2H \\ >C{:}CH\cdot CO_2H \end{cases} \longrightarrow C_7H_{13}\begin{cases} CO_2H \\ >CO \end{cases} \longleftarrow C_7H_{13}\begin{cases} CO_2H \\ CO_2H \\ CO_2H \end{cases}$$

Dehydrohomocamphoric Acid *Camphononic Acid* *Homocamphoronic Acid*

But his characteristic contribution was an idea—an interpretation of the chemistry of camphor which reconciled apparently conflicting data (Brit. Assoc. Rep. Sec. B, Bradford, 1900). In other

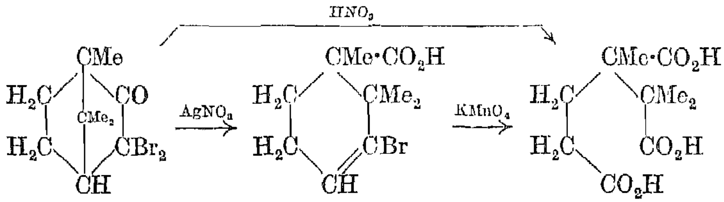
words he saw through the mist and by recognising the occurrence of a remarkable molecular rearrangement in the formation of *iso*lauronolic acid removed the chief stumbling block to the general acceptance of Bredt's camphor formula.



Lauronolic Acid iso*Lauronolic Acid*

The postulated intramolecular change was compared by Lapworth with the pinacol–pinacolone rearrangement and a similar explanation was also applied to the change of α- to β-campholenic acid, which was another source of confusion.

Homocamphoronic acid (III) itself and the stages of its production from αα-dibromocamphor (I) gave a great deal of trouble, as may well be understood when the direct formation of the acid by oxidation of (I) with nitric acid is considered (*J.*, 1899, **75**, 986). A carbon atom seems to get out of place.



(I.) (II.) (III.)

It was shown, however, that Forster's bromocamphorenic acid (II) is probably an intermediate product, and the very remarkable molecular rearrangement, (I) ⟶ (II), was suggested as the result of an extensive series of investigations (*J.*, 1899, **75**, 1134; 1900, **77**, 309, 446; 1902, **81**, 17). Lapworth carried these out in a systematic fashion by the careful study of the properties and reactions of the substances mentioned and, in addition, of camphonic acid, camphononic acid, and various bromo-lactones. It does not seem to have occurred to him to attempt the synthesis of homocamphoronic acid, although that is perhaps due to the fact that the structures became clear only towards the end of a prolonged study.

The examples cited of the mobility of the camphor complex could be supplemented by many others and there is no doubt that the general acceptance of Bredt's formula owed as much to Lapworth's searching analysis as to the eventual synthesis of camphoric

acid. Much later he prepared homocamphor (*J.*, 1920, **117**, 743), but the connecting link with later activities was perhaps his work on cyanocamphor and homocamphoric acid (*J.*, 1900, **77**, 1053). He was led to consider the problem of the addition of hydrocyanic acid to carbon compounds more generally and especially to the $\alpha\beta$-unsaturated ketones and the ketones and aldehydes themselves (*J.*, 1903, **83**, 995; *Proc.*, 1904, **20**, 245; *J.*, 1904, **85**, 1206—1214, 1355; 1906, **89**, 1819, 1869; 1907, **91**, 694, 977; 1910, **97**, 11; *Proc.*, 1911, **27**, 240; *J.*, 1911, **99**, 1877; 1928, 2533; 1930, 1976). The studies ranged from observations of the β-addition of cyano-groups to $\alpha\beta$-unsaturated ketones such as mesityl oxide, benzylidene-acetone, carvone, and pulegone to the later, careful examination of the conditions of formation and the stability of cyanohydrins. There is little doubt that reflection on the mechanism of these reactions played an important part in directing his attention to the principle of "alternate polarities". From the first he adopted ionic mechanisms, and a good illustration of his ideas is seen in the view he put forward of the course of the formation of benzoin from benzaldehyde (*J.*, 1907, **91**, 694). The production of a cyanohydrin was regarded by Lapworth as involving the direct attack of cyanidion on a carbonyl group :

$$>C{=}O \;+\; CN^- \longrightarrow \;>C{<}{}^{O^-}_{CN}$$

This he made very probable by a study of the effect of catalytic agents on the velocity of the addition (*J.*, 1903, **83**, 995) and by showing that the cyanohydrins are complex acids of which he was able to prepare the salts (*J.*, 1904, **85**, 1206). Thus by the action of potassium cyanide on benzaldehyde and camphorquinone he obtained crystalline potassium salts of the cyanohydrins. This view was confirmed by much subsequent research by Lapworth himself, by Bredt, and by Goldschmidt.

The second stage in the formation of a cyanohydrin is the decomposition of water, or an alcohol or acid, by the complex ion.

$$>C{<}{}^{O^-}_{CN} \;+\; H_2O \longrightarrow \;>C{<}{}^{OH}_{CN} \;+\; OH^-$$

He early recognised that these processes must be reversible and that normally an equilibrium will be set up. The theory explained very well why cyanohydrins are so advantageously prepared by the action of pure hydrocyanic acid on a ketone in the (necessary) presence of a small proportion of an alkaline catalyst, which may

be potassium cyanide, or may even be derived from the glass container.

To complete the scheme of the benzoin synthesis it was assumed that benzaldehyde undergoes an aldol-like synthesis with mandelonitrile, and that the cyanohydrin of benzoin is relatively unstable. This was probable on theoretical grounds, and from analogies, but it was also experimentally demonstrated. The complete scheme was (*J.*, 1907, **91**, 694) :

$$C_6H_5\cdot CHO + CN' \rightleftarrows C_6H_5\cdot CH(CN)\cdot O' \quad . \quad . \quad . \quad . \quad . \quad \text{(i)}$$

$$C_6H_5\cdot CH(CN)\cdot O' + H^+ \rightleftarrows C_6H_5\cdot CH(CN)\cdot OH \quad . \quad . \quad . \quad \text{(ii)}$$

$$C_6H_5\cdot CHO + C_6H_5\cdot CH(CN)\cdot OH \rightleftarrows \begin{array}{l} C_6H_5\cdot C(CN)\cdot OH \\ \quad\ \ | \\ C_6H_5\cdot CH\cdot OH \end{array} \quad . \quad \text{(iii)}$$

$$\begin{array}{l} C_6H_5\cdot C(CN)\cdot OH \\ \quad\ \ | \\ C_6H_5\cdot CH\cdot OH \end{array} \rightleftarrows \begin{array}{l} C_6H_5\cdot CO \\ \quad\ \ | \\ C_6H_5\cdot CH\cdot OH \end{array} + HCN \quad . \quad . \quad . \quad . \quad \text{(iv)}$$

It will be noticed that Lapworth postulated reversibility of each stage. The theory has stood the test of forty years and is generally accepted as correct : undoubtedly it represented a landmark in the progress of our understanding of the course of chemical change.

Another outcome of the early camphor period was the use made of optical activity to study the phenomena of desmotropic, or tautomeric, change (*J.*, 1902, **81**, 1491, 1499, 1508; 1903, **83**, 114; 1904, **85**, 46; 1911, **99**, 1785). From the first Lapworth regarded these processes from the ionic point of view first advanced by Brühl in 1899, but in a less explicit form. He, however, greatly extended the conception and supported it by many experimental researches carried on throughout his active career.

Mechanisms were invariably adopted which stressed the fact that the ions, particularly hydrogen ions, must often be regarded as coming in from outside and also as leaving for an unknown, and possibly remote, destination. Thus in keto-enol tautomerism catalysed by acids we have :

$$^{HO}{>}C{=}C{<}^{H} \longrightarrow H^+_{(a)} + {}^{O'}{>}C{=}C{<}^{H} \quad . \quad . \quad \text{(i)}$$

$$^{O'}{>}C{=}C{<}^{H} + H^+_{(b)} \longrightarrow {}^{O}{\gg}C{-}CH_2{-} \quad . \quad . \quad \text{(ii)}$$

where the two protons *a* and *b* are not the same. Although these views, and perhaps some others that he advocated, were not com-

pletely novel, Lapworth made a better combination of them than any other chemist. His consistency and theoretical insight made a great impression on his contemporaries and exercised a powerful influence on the development of organic chemical theory. At a later stage he became interested in the mechanism of esterification and hydrolysis (*Proc.*, 1908, **24**, 100, 152, 153; *J.*, 1908, **93**, 2163, 2187; *Proc.*, 1909, **25**, 20; *J.*, 1910, **97**, 19; 1911, **99**, 917, 1417, 1427, 2242; 1912, **101**, 2249; 1913, **103**, 252; *Proc.*, 1914, **30**, 141; *J.*, 1915, **107**, 857; 1922, **121**, 76). Here again the emphasis was on hydrogen ion catalysis and the theory of acids and complex ions in various media. The researches were developed with the refinements of physico-chemical techniques and cannot usefully be summarised in the course of a short discussion. Many aspects of the work were unfinished and inconclusive but, taken as a whole, it must be admitted that this series of memoirs made an essential contribution to a subject which has excited great interest, and has of course been advanced by many other workers.

Another penetrating suggestion made by Lapworth concerned the mechanism of the bromination of ketones; the case chosen for study was acetone. The rate of bromination was found to be independent of the concentration of bromine and the process was catalysed by acids.

Lapworth suggested that the rate-determining change is the formation of enol from the acetone and that this is immediately brominated. The reaction is therefore autocatalytic due to the accumulation of hydrogen bromide. This view is accepted to-day for the acid-catalysed reaction, but other ions than hydrogen ions play a part and the complexity of the system is illustrated by H. M. Dawson's subsequent examination of the iodination of acetone. Anionotropic as well as prototropic reactions are in evidence. Considering the date (1913) of Lapworth's work (*Proc.*, 1913, **29**, 283) the advance he made was remarkable.

The conception of very rapid bromination of an enol was later utilised by K. H. Meyer for the analysis of mixtures of enols and ketones, for example, ethyl acetoacetate, under various circumstances. Lapworth often told the writer that he ought to have made this ingenious but obvious application. It is, however, doubtful whether full enolisation occurs, and it is not necessary to postulate it. Thus Leuchs has shown that an optically active ketone, the enol of which must be optically inactive, can be brominated without loss of activity. This recalls the observation of

Kuhn and Albrecht that optically active *sec.*-nitrobutane yields an optically active sodium salt. Many other examples of Lapworth's concern with reaction mechanisms could be cited, including his early generalisations of the form of intramolecular changes (*Proc.*, 1895, **11**, 49; *J.*, 1898, **73**, 445; *Proc.*, 1901, **17**, 2; *J.*, 1901, **79**, 1265) and an examination of the synthesis of acetoacetic ester (*Proc.*, 1903, **19**, 189). Moreover he made kinetic studies of many reactions other than those mentioned and his work on the rate of oximation and the properties of oximes (*J.*, 1902, **81**, 549; 1907, **91**, 1133; 1908, **93**, 85) may be given in illustration.

Lapworth discovered many new reactions and transformations of which the following are among the more interesting.

Possibly his investigations of the addition of hydrogen cyanide to unsaturated ketones suggested that the quality of reactivity of the carbon of a carbonyl group can be transmitted to the β-carbon of an αβ-unsaturated ketone. If so, he may have argued, a carbonyl might activate a methylene group through a double bond. At any rate, in 1900 he made an experiment that must have had some such theoretical background.

He found (*Proc.*, 1900, **16**, 132) that ethyl crotonate condensed with ethyl oxalate in the presence of sodium ethoxide as follows:

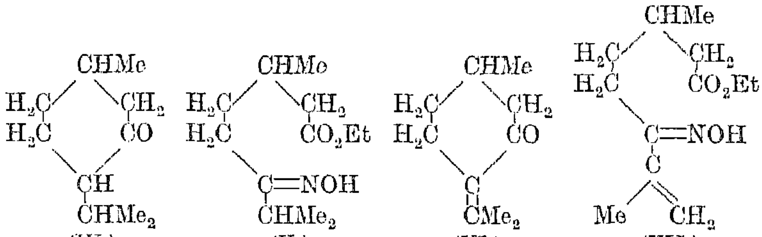
$$CO_2Et{\cdot}CO_2Et + CH_3{\cdot}CH{:}CH{\cdot}CO_2Et \longrightarrow CO_2Et{\cdot}CO{\cdot}CH_2{\cdot}CH{:}CH{\cdot}CO_2Et$$

The constitution of the product has since been confirmed; this was necessary in view of the possibility of the double bond migration to the βγ-position, followed by oxylation in the α-position. An extension was made later (*J.*, 1923, **123**, 1325).

Lapworth and Wechsler (*J.*, 1907, **91**, 1919) noted an anomalous reaction of cyanodihydrocarvone with amyl nitrite in the presence of sodium ethoxide. Further experiments revealed an interesting scission of ketones containing the group $-CO-\overset{|}{C}H-$ under the same conditions. It may be assumed that a nitroso-derivative is first formed and that this adds the elements of alcohol to yield $-CO{\cdot}OEt + HON{:}C{<}$ (*J.*, 1908, **93**, 30).

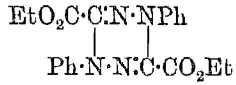
Thus menthone (IV) yields (V) after hydrolysis of the product; pulegone (VI) gives (VII), the process involving the above-mentioned shift of a double bond. A simple model was provided (*J.*, 1911, **99**, 1882) by phenyl *iso*propyl ketone, $Ph{\cdot}CO{\cdot}CHMe_2$, which was found to be converted by amyl nitrite in alcoholic sodium ethoxide into benzoic ester, $Ph{\cdot}CO_2Et$, and acetoxime, $HON{=}CMe_2$. This

reaction has been applied to cinchoninone and affords in this and other cases a useful resource for the ring-fission of ketones.



(IV.) (V.) (VI.) (VII.)

Another degradation was discovered when bromine was allowed to act on ethyl benzeneazoacetoacetate, $CH_3{\cdot}CO{\cdot}CH(N_2Ph){\cdot}CO_2Et$, when the acetyl group was eliminated and a so-called hydrizino-derivative, $CBr(\colon N{\cdot}NHPh){\cdot}CO_2Et$, was produced (*J.*, 1905, **87**, 1854). When treated with alkalis, two molecules condensed to give ethyl diphenyltetrazolinedicarboxylate,



These novel types of substances have not received much subsequent attention.

An interesting paper on sulphonic esters (*J.*, 1912, **101**, 273) describes some new reactions based on the idea that esters and sulphonic esters tend to undergo scission at the dotted line: $R{\cdot}CO \vdots O—R'$, $R{\cdot}SO_2{\cdot}O \vdots R'$. It was found that olefins add the elements of sulphurous acid with the production of sulphonic acids (*J.*, 1925, **127**, 307). In the simplest case ethylene reacts with sodium hydrogen sulphite with formation of ethanesulphonic acid, which was isolated as the barium salt.

$$CH_2\colon CH_2 + NaHSO_3 \longrightarrow CH_3{\cdot}CH_2SO_3Na$$

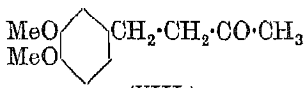
This reaction was rather unexpected; it underlines the abnormality of sulphur and recalls Posner's experiments on the addition of mercaptans to unsaturated substances.

At various times Lapworth paid considerable attention to improvements of preparative methods and to the prescription of satisfactory recipes. For example, he made really pure oleic acid (*Biochem. J.*, 1925, **19**, 7) and studied its quantitative oxidation to

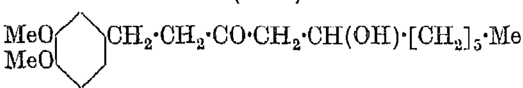
dihydroxystearic acid (*J.*, 1925, **127**, 1628, 1987). This is only one instance of his interest in the chemistry of the fats. He began work on sphingosine and cerebrone (*J.*, 1913, **103**, 1029) but never carried it far.

Other illustrations of the improvement of methods are the reductions of emulsified nitro-compounds (*J.*, 1921, **119**, 765, 768; 1925, **127**, 2970) whereby excellent yields of arylhydroxylamines were obtained, and contributions to *Organic Syntheses* (1927, **7**, 20; 1928, **8**, 99) based on his earlier work with McRae (*J.*, 1922, **121**, 1699, 2741). The details are characteristically elegant. An aldehyde such as benzaldehyde is brought into reaction with sodium cyanoacetate, previously made in the usual way; the addition of hydrocyanic acid and hydrolysis then afford a substituted succinic acid.

An unusual development for Lapworth was a study of natural products, in this case the pungent principles of ginger (*J.*, 1917, **111**, 77) and capsicum (*J.*, 1919, **115**, 1109). It is curious that E. K. Nelson, and also H. Nomura, published work on gingerol almost simultaneously with that of Lapworth, Pearson, and Royle. The work of Lapworth and his collaborators was the most comprehensive. The oleo-resin of Thresh, and of Garnett and Grier, methylated by means of methyl sulphate and alkali, yields a crystalline compound termed methylgingerol. This is decomposed by heat or alkali into methylzingerone, $C_{12}H_{16}O_3$, and aldehydes, of which the chief is *n*-heptaldehyde. Methylzingerone was proved by analysis and synthesis (*J.*, 1917, **111**, 790) to be β-veratrylethyl methyl ketone (VIII) and the most plausible view of methylgingerol is expressed by the constitution (IX).



(VIII.)

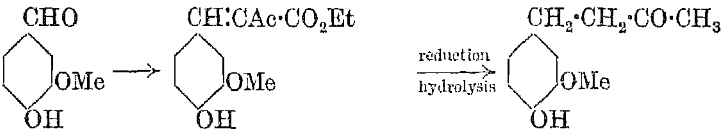


(IX.)

Similarly the oleo-resin, before methylation, gave zingerone, $C_{11}H_{14}O_3$, which was proved by synthesis to be (X).

When, in the early Manchester days, one discussed synthetical projects with Lapworth, it was quite clear that he had some unusual way of deciding whether they would " go " or not. It turned out

to be a scheme of alternating polarities in a chain of atoms, and the theory was published in 1920. Although somewhat hidden in the *Memoirs of the Manchester Literary and Philosophical Society* (lxiv, No. 3, 1), the paper evoked much interest, and not a little criticism. In later publications the theoretical basis was broadened



(X.)

and the principle developed with a conception of " virtual valencies " (*J.*, 1922, **121**, 416). Unfortunately this method of treatment was difficult to assimilate because of its form and, as the electronic interpretations, really equivalent to Lapworth's, were gradually adopted generally, this memoir of 1922 was almost forgotten.

Lapworth's main contribution to modern theory was his classification of reagents and his earlier work on reaction mechanisms, which were closely inter-related.

Starting from the two ionic types, he termed groups and molecular centres that exhibit reactive properties analogous to anions, *anionoid*, and those behaving like cations, *cationoid*. These expressions have exactly the same meaning as Ingold's *nucleophilic* and *electrophilic*. They implied electron donors, and electron acceptors, respectively. In regard to a few misconceptions, which arose in discussions, let Lapworth speak for himself (citations from *Mem. Manchester Lit. Phil. Soc.*, *loc. cit.*). " The writer originally fell into the habit of labelling the atoms in reactive molecules with + and − signs as the result of his applications of the ionic theory to the reactions of carbon compounds and especially to those of ketones and allied carbonyl compounds. . . . It must be emphasised, however, that in attaching the + and − signs to the oxygen and carbon atoms no hypothesis is invoked, nor is it necessary, or even desirable, to assume that electrical charges are developed on these two atoms (except perhaps at the actual instant of chemical change). The signs are applied, in the first instance, merely as expressing the relative polar characters which the atoms seem to display at the instant of the chemical change in question." He clearly distinguished his views from the earlier theories of Fry and Vorländer which, more precisely in the case of Fry, did postulate actual alternate electric charges.

An example given was :

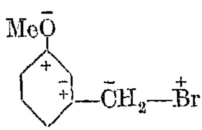
$$\text{“ } 2\bar{C}H_3\cdot\overset{+}{C}H{:}\bar{C}H\cdot\overset{+}{C}H\bar{O} \longrightarrow \bar{C}H_3\cdot\overset{+}{C}H{:}\bar{C}H\cdot\underset{\underset{-\ +}{OH}}{\overset{+}{C}}H\cdot CH_2\cdot\overset{+}{C}H{:}\bar{C}H\cdot\overset{+}{C}H\bar{O} \text{ ”}$$

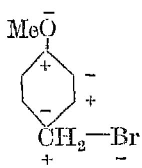
"It must now be evident from [corrected in reprints to *in*] the cases already dealt with that the whole order of alternating latent polarities is determined by the oxygen atom or atoms. . . . The extension of the influence of the directing, or *key-atom*, over a long range seems to require for its fullest display the presence of double bonds, and usually in conjugated positions, consequently the principle must find ample scope in the aromatic series where conjugation is the rule."

It was this aspect which was emphasised in the paper of 1922 (*J.*, 1922, **121**, 416) and the views there developed are, to all intents and purposes, identical with those advanced by the present writer starting from the conception of partial valencies. Both had some analogies with the systems of Thiele and of Flürscheim and in some applications gave identical results. There was seen to be divergence, however, in other important respects and the origin of these became clear with the development of translations into the terms of the electronic theory of valency.

The working hypothesis of " labelling " from a key-atom gave rise to some interesting experimental work and an early example is that of Lapworth and Shoesmith (*J.*, 1922, **121**, 1391) on the methoxybenzyl bromides.

Thus the *m*- and *p*-isomerides are labelled from oxygen as key-atom :





The behaviour of these substances was found to harmonise with that predicted from the figures. It was known that Br in, for example, $\bar{O}{=}\overset{+}{C}{-}\bar{B}r$ is very readily replaced by OH and that Br in $\bar{O}{=}\overset{+}{C}{-}\bar{C}H{-}\overset{+}{B}r$ is unusually readily replaced by H. *p*-Methoxybenzyl bromide was much more easily hydrolysed to the related

alcohol than was *m*-methoxybenzyl bromide, and in reductions to the tolyl methyl ethers, the *m*-isomeride was the more reactive.

Nowadays the properties of the *p*-derivative can be readily interpreted on a more precise electronic basis, but the *m*-derivative would be regarded as a benzyl bromide, lacking the special constitutive features of the *p*-type, and differing from benzyl bromide itself only as the result of the general electrical effect of the methoxy-group. In other words, it is the *p*-derivative that exhibits exceptional behaviour, and a comparison of benzyl bromide and *m*-methoxybenzyl bromide is required in order to estimate the significance of the contrast to which Lapworth and Shoesmith drew attention.

About this period (1922—26) an active controversy arose (cf. *J.*, 1925, **127**, 1742); this consumed much time and effort but need not be described in detail. Lapworth himself would be the last to desire these ephemeral writings to be resuscitated on account of their purely historical interest. It had at least one useful result in that the theory was more quickly moulded into its present form.

The chief subsequent events have arisen from the applications of quantum mechanics to organic chemical problems. These have provided a new calculus for the electronic theory of valency but have not rendered the older qualitative approach obsolete.

Lapworth's last scientific paper (*J.*, 1931, 1959) was most happily a collaborative effort with Professor C. K. Ingold. It was concerned with the problem of *m*-nitration of toluene. Competitive nitrations of toluene and benzene show that toluene is far more readily attacked than benzene. But in the nitration of toluene, only 4·4 per cent. of the *m*-derivative is produced. The question arises—does the methyl group activate the *m*-position, relative to the reactivity of benzene? Careful experiments showed that this is indeed the case, the disparity of toluene and benzene reactivity being sufficient.

There is little doubt that Lapworth would have continued to shed light on these and similar problems but unfortunately signs of his illness made their appearance early in the third decade of the century. He continued for some years to inspire his colleagues and collaborators by discussion and correspondence. Indeed it is true to say that throughout his life, though his publications are highly important, his generous help to others had an almost equal, if not greater, influence on the progress of science.

The world-wide recognition of Lapworth's genius and his abiding

scientific reputation increases with the passage of time. It is now seen that his insight into chemical mechanisms, and his insistence on the electrochemical point of view at the molecular level, forged a necessary link in the chain of theory which now connects the most diverse phenomena.

In the laboratory one of his students, Dr. G. N. Burkhardt, gives the following picture. "He was skilful in devising and using the simple methods which he always preferred and, with a home-made cigarette in one corner of his mouth, and his head on one side, he would attack a new substance with reagents and a set of test-tubes. Using traces of material and a number of uncommon devices, he would find as much in a few minutes as might take hours to establish on a larger scale with more elaborate technique. As a teacher, lecturing on three main branches of chemistry in succession, he concerned himself to an unusual degree with the exposition of ideas, methods, and general principles, so that his lectures were most stimulating and valuable to his better students, though they could be the despair of those whose tastes or abilities required only the easy catalogue of facts."

In his dealings with his fellow men he was selfless, generous to a fault, and completely straightforward and sincere. His scientific work occasionally brought him into controversy with exponents of older views, but this was always conducted with great dignity and the most careful choice of words. Incidentally he possessed an enviable command of language especially noticed in his writing, and a pretty and sometimes caustic wit, entirely free from any suspicion of malice. As administrator of his department and laboratory he showed firmness and wisdom, but this was not his real *métier* and it is a pity that a sense of duty compelled him to undertake responsibilities which turned out to last far too long. As already mentioned, the valuable help of Mrs. Lapworth lightened the load of routine for several years. The loyalty with which Lapworth was served and the undying devotion of all those who collaborated with him whether in teaching or research are the best testimony to his professional work and the University of Manchester owes much to his encouragement of young men of promise and to his guidance of the School of Chemistry during critical years.

A sensitive soul, always sparkling with vitality, all-embracing in his curiosity and interest, it is natural that he had many hobbies.

His father was a pianist and his mother and sister were accom-

plished singers. He himself played the violin and 'cello and was a lover of music, with sound and individual taste and a wide knowledge of the classics. He had little use for the modern forms. At New Cross he took part, as violinist, in chamber music and played in the College orchestra. When he came to Manchester, Perkin asked him to share in his famous musical parties but there were too many violinists and Lapworth learned the viola. For many years he served on the Council of the Royal Manchester College of Music. He was a good dancer, was fond of the theatre, of films, radio, and the gramophone, and, in my time, he was a voracious reader of thrillers. Carpentry and microscopy were just two of his pursuits, and outside his chemistry his main scientific interests were astronomy, geology, and botany. He was an authority on British mosses and made a fine collection of them.

Holidays were spent in mountaineering and later in golfing and fishing. As a boy he started scrambling at St. Andrews and soon accompanied his father on geological expeditions to the mountains. At the age of eighteen he made a solitary ascent of the Petit Dent de Veisivi and later climbed Lliwedd and the Rosenlaui Engelhörner by several routes.

Much affected by the loss of his friend Humphrey Owen Jones and his wife on the Aiguille Blanche de Peteret, he never climbed again.

His fishing ground was chiefly the river Eden near Gosforth, and he was a member of the Yorkshire Anglers Club. Speaking of one of his friends he said: "The keenest angler I know—what a pity that he never catches fish".

The outdoor life consorted well with his interest in nature, and it was K. J. P. Orton who introduced him to the study of birds. Orton, a recognised authority, was good with the field-glasses, but Lapworth's trained and sensitive ear enabled him to surpass his teacher in the recognition of birds by song. Birding with the Ortons was the *raison d'être* of many happy expeditions round Hayes Common, Keston, and in the Bangor district. Many years later the writer found in a St. Andrews "den" that Lapworth had not forgotten his craft.

The breadth of interest and joy in life which Lapworth showed in his recreations were characteristic of the man. In science, too, his temperament might have caused too wide a spread, but he was saved from this by self-discipline and by a dominant theoretical theme.

Lapworth's health, at least in later years, was never robust, and the exceptional strain of carrying the burden of the whole Department of Chemistry eventually broke it down. His long and distressing illness was borne with the greatest fortitude but, until the very end, he never lost his interest and was able to enjoy the visits of his friends at intervals.

J. F. THORPE

JOCELYN FIELD THORPE

1872—1940

By the death, on June 10th, 1940, of Sir Jocelyn Thorpe, the profession of Chemistry lost one of its outstanding figures and the Chemical Society a devoted supporter who had served it as Treasurer, Vice-President, and President, and a large circle of friends were left to mourn a remarkably kind, genial, and hospitable personality.

Jocelyn Field Thorpe was born on December 1st, 1872, and was the sixth son of the late William George Thorpe, F.S.A., a barrister-at-law of the Middle Temple. Thorpe's father had been educated at Cambridge in the classical tradition; but he was a man of liberal outlook and ready to encourage his son in the independent choice of a career.

After receiving his earliest education at a preparatory school near his home in Clapham, Thorpe went at the age of ten to Worthing College. He showed considerable aptitude for games in spite of having one leg shorter than the other, the result of infantile paralysis in his childhood, and was particularly good at cricket. He specialised in wicket-keeping and retained his love of the game to the end. His holidays were spent on his father's estate in Devonshire, where he learnt to shoot and fish with his brothers.

After leaving school in 1888, he returned to London to study Engineering at King's College. He derived much benefit in later life from this early training, particularly from the practical work in the machine shops of Alexander Wilson's works at Vauxhall, where he worked during the Long Vacation. However, Engineering was not his true vocation, and at the end of two years he abandoned it for Chemistry. The change was made on the advice of his namesake, Sir Edward Thorpe, whom Thorpe's father consulted; this was a bold step at a time when the profession of Chemistry still lacked, in this country, the recognition it was to win in later years.

Thorpe entered the Royal College of Science at South Kensington in 1890 and took the first year's course in elementary Chemistry and Physics, and in the following year advanced Chemistry, mainly

Organic. In 1892, following Sir Edward Thorpe's advice, he went to Heidelberg, where, at that time, the faculty of Science was second to none. Bunsen was still there, although he had retired; other famous men were Victor Meyer, Auwers, Jannasch, Gattermann, Brühl, Horstmann, Krafft, and Knoevenagel, the physicist Quincke, and the equally celebrated mineralogist Rosenbusch. The number of English students at Heidelberg was considerable; amongst Thorpe's contemporaries were J. F. Bottomley, G. C. (later Sir Christopher) Clayton, J. C. Cain, J. N. Goldsmith, J. T. Hewitt, J. McRae, B. (later Sir Bernard) Pares, T. S. Patterson, and J. H. Wigner. There was a fair-sized English colony and Thorpe was welcome in many houses; he took part in theatricals and played cricket and lawn tennis. With so many distractions Thorpe did not work particularly hard until shortly before the examinations; then he would retire to the Black Forest, and come back to give a good account of himself. He took his degree in 1895; his Doctor's thesis, carried out under Auwers's guidance, dealt with the $\alpha\alpha'$-dimethylglutaric acids and was an excellent piece of work. Thorpe returned to Heidelberg for the summer of 1897, but devoted his whole time to the study of dyes and dyeing at the Badische Works at Ludwigshafen.

On obtaining his degree at Heidelberg, Thorpe returned to England and joined the great research school at Manchester University, where W. H. Perkin, jun., was then at the height of his fame. Here Thorpe found his true vocation; he worked hard and his enthusiasm was amply rewarded by results. He soon took the degree of D.Sc. and was appointed Lecturer in Organic Chemistry with special charge of a course, both theoretical and practical, on dyes and dyeing, which was particularly successful. The practical work was conducted in Thorpe's private laboratory, at that time a shed in the back quadrangle, a part of which he had fitted up for research; he generally had one research student working there. However, he kept in constant touch with Perkin in the main building and thus arose a productive collaboration extending over many years. Those who remember this period speak of Thorpe's excellence as a teacher, but especially of his great skill as a manipulator and of the delight he took in practical work. Although the work of Perkin's school was mainly concerned with the structure of natural products, Thorpe's own approach to these problems was almost entirely from the synthetic side and he took comparatively little interest in their analytical aspect. A fitting recognition of Thorpe's distinguished

work at Manchester came with his election to the Royal Society in 1908.

During the early part of his stay in Manchester Thorpe shared rooms with the late Dr. J. C. Cain, and it was then that the project of their well-known treatise on synthetic dyes first took shape.

In 1909 Thorpe was appointed Sorby Research Fellow of the Royal Society and moved to Sheffield, where he spent a fruitful period of his career. He had a pleasant and well-equipped laboratory and no teaching duties, and could devote the whole of his time to research with the aid of an assistant. He did much of the practical work himself, keeping his assistant very busy carrying out analyses and preparing large amounts of starting materials, although he always discussed his plans and published his work in collaboration with the assistant. He liked working on a generous scale when tackling a synthetic problem, although his mastery of technique often enabled him to take a short cut to the required product. He worked hard, allowing himself, perhaps, a round of golf on Sunday by way of relaxation.

In 1913 came Thorpe's great opportunity: he was appointed to the Chair of Organic Chemistry at the Imperial College of Science and Technology in London and began his duties there early in 1914. He brought to his new task a contagious enthusiasm and this, combined with his great gifts as a lecturer, had an immediate vitalising effect on his Department. He attracted an eager band of pupils anxious to do research; but his first step was to try to improve the somewhat inadequate facilities then available, and this was in part achieved by the end of the summer.

The writer has vivid recollections of Thorpe during this period: he was full of ideas, which were always stimulating and greatly added to the interest of his lectures; in the laboratory he worked with gusto and delighted in such operations as the preparation of "molecular" sodium; he would often try a reaction on a small scale, always working in test-tubes (he even contrived to carry out extractions with ether in test-tubes), and leaving his students to repeat it on a larger scale if it turned out promising; he was seldom without a cigarette—sometimes a cigar—and generally in shirt sleeves, and had a habit of propping up test-tubes in drawers or against gas-taps. A characteristic attitude of Thorpe in the laboratory is portrayed in the accompanying photograph.

All plans of expansion were brought to an end by the outbreak of the First World War. Thorpe immediately set about making the

best possible use of the facilities and men available at South Kensington and started the manufacture of drugs—principally phenacetin, novocaine, and β-eucaine—which had until then been imported from abroad. War work, such as the investigation of war gases, explosives, etc., claimed more and more of his time. He became a member of the Trench Warfare Committee and carried out much experimental work, a good deal of it in collaboration with Dr. M. A. Whiteley, who was a member of his staff.

Teaching still went on; and in 1919 Thorpe was at last able to realise his ambition of founding a great research school. There was a large influx of research students in the years immediately following and a constant expansion of research accommodation; where two assistants had worked in 1914, some thirty research students and junior members of staff were housed by 1921. The number of members of staff was increased, notably by the creation of a post connected with the newly-founded Whiffen Laboratory. This laboratory had been built and equipped by the late William Whiffen and contained a representative selection of large and semi-large scale apparatus, where students could be taught the practical uses of plant; the first lecturer was C. K. Ingold, later followed by E. H. Farmer. Thorpe also had a private assistant, supported by a grant from the Department of Scientific and Industrial Research; the assistant's duties were, however, nominal and allowed him to devote his whole time to research.

By this time Thorpe had so much to do that he was no longer able to carry out experimental work himself, a circumstance he often regretted; but he was always ready to listen to anyone in difficulties and to give them advice; a favourite piece of advice was "try the unlikely", and he was never stereotyped in his suggestions. Characteristically, too, he seldom had his name included in the publications of his staff, although he took a great interest in them.

After 1919 Thorpe took an increasing share of public duties, as was inevitable for one of his ability and shrewd judgment. The first task of importance which fell to him was to preside over the Indian Chemical Services Committee; he spent some months in India in 1919, and did more than his share of the work of the Committee, being largely responsible for the report, which, however, hardly found the recognition it deserved; he himself regarded the time spent in India largely as wasted, except in so far as it served to bring him in contact with chemists there. He had a succession of Indian students from 1919 onwards as the result of his visit.

Thorpe remained a member of the Chemical Defence Committee until it was reconstituted in 1939, and received the C.B.E. in 1917. He gave much of his time and thought to the Advisory Council of the Department of Scientific and Industrial Research, on which he served from 1916 until 1922. He became scientific adviser to the Anglo-Persian (now Anglo-Iranian) Oil Co. and undertook a trip to Persia in 1929. He was also a member of the Advisory Board of the Dyestuffs Group of Imperial Chemical Industries from 1929 until his death, and of the Safety in Mines Research Board (1924—35), Chairman of the Explosives in Mines Committee, Department of Mines, a member of the Dyestuffs Development Committee of the Board of Trade (1925—34), and served on the Royal Society's Council (1923—25). He was president of the Institute of Chemistry from 1933 to 1936.

Thorpe's services to the Chemical Society, which he joined in 1893, deserve more than passing comment. From his arrival in London he took a prominent part in the work of the Society. He served on the Council from 1915 to 1918 and became a Vice-President in 1921; in the following year M. O. (later Sir Martin) Forster relinquished the post of Treasurer, and Thorpe succeeded him, remaining in that capacity until he was elected President in 1928. During that time the Society was passing through a particularly difficult period: the receipts were barely sufficient to cover the cost of the Society's publications, and Thorpe set himself the Herculean task of tapping fresh sources of income. He founded the Publications Fund with this end in view, having always maintained that the Society's primary function was the publication of new knowledge. He very early conceived the idea of co-ordinating the various chemical bodies in the country and so preventing the inevitable overlap of their functions and consequent waste. He took an active part in the Association of Scientific and Technical Societies, which had similar aims. After years of patient work the Scheme of Co-operation was ripe, only to be shelved owing to the financial depression of 1931. It was owing to his connection with this scheme that he was asked to serve as President for an additional year (1930—31); it is satisfactory to note that, although the original scheme did not materialise, a variant of it is now in operation. He became the first Treasurer of the Chemical Council. During his Presidency Thorpe commissioned Herbert Budd to paint the fine portrait of the first President, Thomas Graham, which now hangs in the Society's rooms, and headed the subscription for it.

The Chemical Society honoured Thorpe by the presentation of the Longstaff medal in 1921 and the Royal Society presented him with the Davy medal in the following year; he received a knighthood in 1939 for his valuable public services.

On his retirement from the Imperial College in 1938 Thorpe devoted himself to the task of editing, in collaboration with Dr. M. A. Whiteley, the "Dictionary of Chemistry" started by Sir Edward Thorpe.

Thorpe married in 1902 Lilian, the daughter of the late William Briggs, J.P., of Hale, Cheshire. Lady Thorpe took a full share in her husband's career; she accompanied him on his trips abroad, helped him to entertain and so maintain his many contacts, and nursed him with devotion and firmness when his health began to give way. Many will remember the Thorpes' kindly hospitality at their house in Chelsea, amongst the fine collection of English porcelain of which Thorpe was a great connoisseur; Thorpe himself was a charming host and a discerning judge of wine and cigars.

Although he was always a good lecturer, it is said that he was not a particularly good public speaker until well on in his career. In the last fifteen years he was certainly first-rate, spontaneous, interesting, and with a pleasantly light touch.

It is something of a paradox, in one so kindly and genial as Thorpe, that he was reticent and never talked about himself. His kindness was probably his outstanding feature; he always believed the best of everyone, and this was, indeed, occasionally a source of embarrassment to his staff in their efforts to maintain discipline. He was cheerful and good-tempered, with a liking for the good things of life, and a lively sense of humour. He enjoyed telling a story against himself, emphasising the point with that characteristic "h'm?"—half-grunt and half-chuckle—that his friends knew so well.

Distinguished as were Thorpe's scientific achievements and great as were his services both to Chemistry and to the Chemical Society, it is perhaps his kindliness and humanity that will remain longest in the memory of those who knew him.

The Scientific Work of Jocelyn Field Thorpe.

Thorpe's chemical researches were carried out during the forty-year period from 1894 to 1934 in the Universities of Heidelberg, Manchester, Sheffield, and London. During this period he wrote 120

original memoirs, in addition to minor material. With two exceptions, his papers were published in the *Journal* of the Chemical Society.

His scientific life falls naturally into four periods. During roughly the first decade he was learning his chosen subject and acquiring "the tools of his trade", partly from K. Auwers and W. H. Perkin, jun., but mainly by prolonged and arduous work in the laboratory. In this way he acquired the mysterious "feeling" for compounds and reactions which characterises the more gifted organic chemists. Then he entered upon a great period of research from 1904 until 1914. There followed the Four Years' War, during which other duties stopped his academic work. With the end of the war Thorpe devoted himself to making the Imperial College a centre of research for organic chemistry. Students came to South Kensington from all over the world, and there ensued the second "flowering period" in Thorpe's life, which culminated in the vast activity of the years 1922 and 1923. Thereafter the call of administrative duties and his work for the Government, the Chemical Society, and the profession of Chemistry in general took up more and more of his time. He reconciled himself to exercising a general benevolent supervision over the research work of his department, although he remained actively interested in some of his favourite subjects until his retirement.

When Thorpe entered upon his career, organic chemistry was in the full tide of its extraordinary expansion in Germany, England, and France. It was perhaps inevitable for one of his character and abilities to become attracted to this branch of chemistry, and to it he remained faithful throughout his long career. At times he used the tools of physics to obtain results which interested him, but on the whole his attitude towards physical chemistry was one of genial tolerance. It is more remarkable that, with a few exceptions, his own experimental work had little direct contact with biology. This is probably due to the fact that, when once he had embarked upon his life work, he was caught up in a maelstrom of activity which took up his full attention and completely satisfied his scientific instincts.

Thorpe's activities in organic chemistry were many-sided. At the outset of his career his powerful and receptive mind was influenced by the varied activities of Perkin's laboratories at Manchester. In later life we find him picking up and developing lines of work suggested by his early experiences. Certain themes, indeed, run

throughout his whole work: his interest in polybasic acids, dating back to his Heidelberg days, in tautomerism, arising from his first researches on cyanoacetic ester, and, perhaps above all, in the complexities of alicyclic rings, are three examples. The review which follows is not strictly historical, but illustrates the development of the various main themes.

1. *Synthesis and Properties of Saturated Polybasic Acids.*

The problem assigned by Auwers to Thorpe for his doctorate research was the study of the trimethylsuccinic and dimethylglutaric acids. Zelinsky had reported the existence of two isomeric inactive trimethylsuccinic acids, whereas only one is required by stereochemical theory. Thorpe was able to show that Zelinsky's second acid was in fact a mixture of the two stereoisomeric $\alpha\alpha'$-dimethylglutaric acids (m. p. 140° and 127°). Moreover, the substance previously described as $\alpha\alpha'$-dimethylglutaric acid (m. p. 101°) was also a mixture of these two stereoisomerides. Zelinsky's acid had come from the hydrolysis of the condensation product of α-bromo*iso*butyric ester and sodio-α-cyanopropionic ester. The abnormal formation of the glutaric derivative was due to an elimination of hydrogen bromide, followed by an addition of the sodioester to the double bond so formed.

A similar condensation engaged Thorpe's attention after his arrival at Manchester. In his first paper with W. H. Perkin he showed that α-bromo*iso*valeric ester condensed normally with sodiomethylmalonic ester in boiling xylene. Hydrolysis of the product yielded *cis*- and *trans*-methyl*iso*propylsuccinic acids. The same acids were obtained when α-bromo*iso*valeric ester was condensed with sodiomalonic ester and the product methylated and hydrolysed (Bentley, Perkin, and Thorpe, *J.*, 1896, 69, 270). During these researches Thorpe became familiar with the technique of the Conrad–Guthzeit method and with the preparation of anhydrides from dibasic acids. These were later to affect his method of attack on the problems of glutaconic acid chemistry.

Thorpe became interested in the differences between the sodium derivatives of cyanoacetic and malonic esters. In 1900 he published a group of three papers (one with Young, one with Howles and Udall) on this point and on the use of cyanoacetic ester in synthesis. He observed that sodiocyanoacetic ester is considerably more stable than sodiomalonic ester and that its aqueous solution does not

develop an alkaline reaction but, on evaporation, yields sodium cyanoacetate. He suggested that the reaction proceeded:

$$CN{\cdot}CH_2{\cdot}CO_2Et \longrightarrow CN{\cdot}CH{:}C{<}^{OEt}_{ONa}$$

$$\downarrow$$

$$CN{\cdot}CH_2{\cdot}C\begin{matrix}\diagup OH\\ -OEt\\ \diagdown ONa\end{matrix} \longrightarrow CN{\cdot}CH_2{\cdot}C{<}^{O}_{ONa}$$

This was correlated with the formation of large quantities of acid esters during the addition of sodiocyanoacetic ester to unsaturated esters in alcohol, which was attributed to the process:

$$CO_2Et{\cdot}CH{:}CR_2 + CH(CN){:}C{<}^{OEt}_{ONa}$$

$$\downarrow$$

$$CO_2Et{\cdot}CH_2{\cdot}CR_2{\cdot}C(CN){:}C{<}^{OEt}_{ONa}$$

$$\downarrow{\scriptstyle H_2O}$$

$$CO_2Et{\cdot}CH_2{\cdot}CR_2{\cdot}CH(CN){\cdot}C\begin{matrix}\diagup OH\\ -OEt\\ \diagdown ONa\end{matrix}$$

$$\downarrow$$

$$CO_2Et{\cdot}CH_2{\cdot}CR_2{\cdot}CH(CN){\cdot}C{<}^{O}_{ONa}$$

In the course of his paper with Howles and Udall (*J.*, 1900, **77**, 942) Thorpe describes an important discovery, the value of which was not realised at the time. A quantity of ethyl α-methylacrylate was prepared from ethyl α-bromo*iso*butyrate and diethylaniline. Thorpe says of the product, "The clear mobile liquid passing over between 117° and 120° consists of pure ethyl α-methylacrylate; it must at once be used, however, since on standing it slowly polymerises to a white, transparent substance resembling gelatine." It was not until more than thirty years later that this "white, transparent" polymeride of methacrylic ester was recognised as a valuable substitute for glass ("Leukon," "Diakon").

The separation of the "*cis*" and the "*trans*"-forms of these substituted glutaric acids was an important practical problem, and Thorpe introduced a new method for this purpose in 1903 (*J.*, **83**, 351).

Thorpe made two important general contributions to the methods

available for the preparation of dibasic acids. One for the preparation of β-substituted glutaric acids will be more suitably considered later. The other was described in a paper with Miss Higson (*J.*, 1906, **89**, 1455). It was observed that sodiocyanoacetic ester readily condensed with the cyanohydrins of aldehydes and ketones; hydrolysis of the product yielded the corresponding succinic acid:

$$\underset{\textstyle CN}{R_2C{\cdot}OH} + \underset{\textstyle CN}{CHNa{\cdot}CO_2Et} \longrightarrow \underset{\textstyle CN}{R_2C}{-}\underset{\textstyle CN}{CNa{\cdot}CO_2Et} \quad (I.)$$

$$\downarrow$$

$$\underset{\textstyle CO_2H}{R_2C}{-}CH_2{\cdot}CO_2H$$

Moreover, the condensation product (I) could be alkylated, and in this way a large range of substituted succinic acids became available. The yields by this process are very good (65—95%), and the method has passed into general use for preparative purposes.

2. *Investigations relating to Camphor and other Terpenes.*

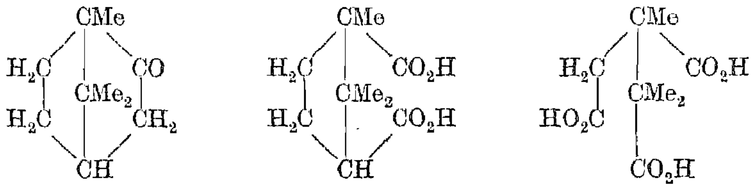
When Thorpe joined Perkin at Manchester, the problem of the structure of camphor was attracting the attention of organic chemists all over the world and was still far from solution. It was as if in this small enigmatic molecule Nature had thrown down a challenge to chemists. The structure of camphor seems to have had at that time a symbolic significance which transcended even the value of the actual scientific truth. At all events, there was a tremendous concentration of chemical talent on this single problem.

Perkin used entirely the synthetic approach, of which he was rapidly becoming a master. In 1896 some early experiments were directed, with Thorpe's assistance, towards the synthesis of camphoric acid. In the following year (*J.*, 1897, **71**, 1169) Perkin and Thorpe announced the synthesis of inactive camphoronic acid. For a proper appreciation of this feat it will be convenient to review briefly some aspects of the state of camphor chemistry at the time.

Camphor was known to be a monoketone, $C_{10}H_{16}O$. It was saturated and therefore dicyclic. Its oxidation with nitric acid was known to yield successively camphoric, camphanic, and camphoronic acid:

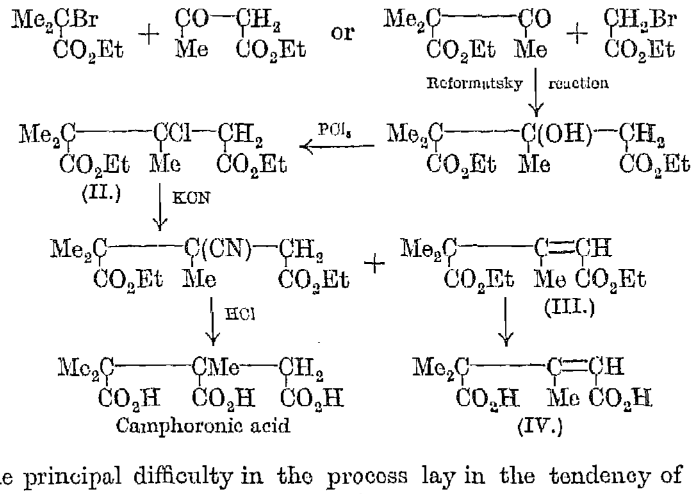
$$C_{10}H_{16}O \longrightarrow \underset{\text{Camphoric acid}}{C_{10}H_{16}O_4} \longrightarrow \underset{\text{Camphanic acid}}{C_{10}H_{16}O_5} \longrightarrow \underset{\text{Camphoronic acid}}{C_9H_{14}O_6}$$

Bredt had shown that camphoronic acid was a tribasic acid and yielded trimethylsuccinic acid and *iso*butyric acid on destructive distillation. This led him to propose, in 1893, the following (now accepted) formulæ:



Camphor Camphoric acid Camphoronic acid

Tiemann (1895), however, rejected these and proposed alternatives, including the formula $CO_2H{\cdot}CHMe{\cdot}CMe_2{\cdot}CH(CO_2H)_2$ for camphoronic acid. This found little favour because of the fact that the acid can be distilled in a vacuum without decarboxylation. Nevertheless there was little positive evidence in favour of Bredt's formulæ, and it was to confirm this that the Perkin–Thorpe synthesis was undertaken. This classical series of reactions is so well known as to require no comment here. It is given in outline below:

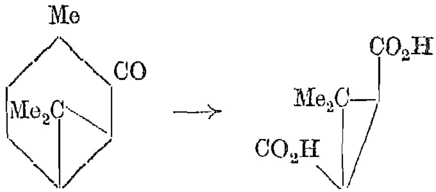


The principal difficulty in the process lay in the tendency of the chloro-ester (II) to give trimethylglutaconic ester (III) on treatment with alkali cyanide, so that the final hydrolysis product contained far more of the unsaturated acid (IV) than of the desired camphoronic acid. However, the latter was isolated by means of its sparingly

soluble barium salt. It was identical with the inactive acid which Aschan had made two years previously by mixing equal parts of *d*- and *l*-camphoronic acids, prepared from natural sources.

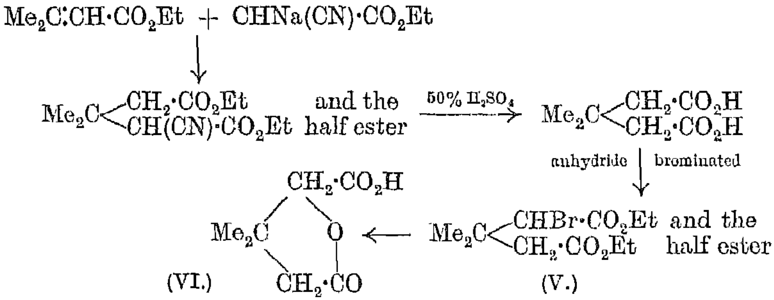
Occasion was taken to examine the trimethylglutaconic acid (IV), which was formed in large amounts as a by-product—an accidental circumstance which probably had a considerable effect on Thorpe's subsequent researches. The high resistance of the acid to bromine, permanganate, and reducing agents was noted. The corresponding *iso*- or *cis*-acid gave an anhydride with remarkable ease, even when the acid was dissolved in hot water and the solution allowed to cool.

Two years later Perkin and Thorpe synthesised the caronic acids (*J.*, 1899, **75**, 48), which Baeyer and Ipatieff had prepared by oxidising carone with permanganate at 100°.



Caronic acid,
cis- and *trans*-forms.

The synthesis was as follows :



α-Bromo-ββ-dimethylglutaric ester (V) on treatment with hot alcoholic potash yielded caronic acid (mainly *trans*-) and the lactonic acid (VI). The half ester of the bromo-acid yielded *trans*-caronic acid alone.

In the same year Perkin and Thorpe were successful in synthesising αββ-trimethylglutaric acid and in proving its identity with the acid obtained by the complete reduction of Balbiano's acid, $C_8H_{12}O_5$.

The latter had been obtained by the oxidation of camphoric acid with permanganate. It was to claim Thorpe's attention again in later years.

Encouraged by these successes, Perkin and Thorpe attempted the much more difficult task of synthesising camphoric acid. In 1903 (*Proc.*, **19**, 61) they gave the preliminary, and in 1904 the complete account (*J.*, 85, 128) of their investigations. In the interval between the appearance of these reports Komppa sent the first description of his brilliant synthesis of camphoric and dehydrocamphoric acids to the *Berichte* (1903, **36**, 4332).

Perkin and Thorpe proceeded as follows:

$$CH_2{:}CH{\cdot}CO_2Et + CHNa(CN){\cdot}CO_2Et \longrightarrow CO_2Et{\cdot}CNa(CN){\cdot}CH_2{\cdot}CH_2{\cdot}CO_2Et$$

$$\big\downarrow + CMe_2Br{\cdot}CO_2Et$$

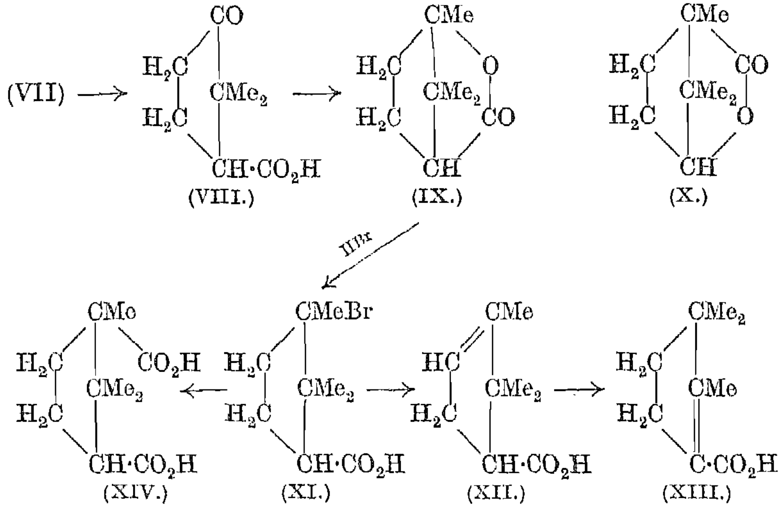
$$\underset{\textstyle CMe_2{\cdot}CO_2H \quad (\text{VII.})}{CO_2H{\cdot}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H} \xleftarrow{\text{hydrolysis}} \underset{\textstyle CMe_2{\cdot}CO_2Et}{CO_2Et{\cdot}C(CN){\cdot}CH_2{\cdot}CH_2{\cdot}CO_2Et}$$

The sodium salt of the acid (VII) was heated with acetic anhydride to yield the keto-acid (VIII). The corresponding ester on treatment with methylmagnesium iodide gave α-campholactone (IX), isomeric with the campholactone (X), which had already been obtained from natural sources.

Treatment of the lactone (IX) with hydrogen bromide gave the bromo-acid (XI), which on successive treatment with sodium carbonate and dilute sulphuric acid gave (inactive) α-campholytic acid (XII) and *iso*lauronolic acid (XIII), the latter being identical with that prepared from " natural " camphoric acid.

Perkin and Thorpe also attempted the conversion of the bromo-acid (XI) into camphoric acid (XIV) by treatment with potassium cyanide, followed by hydrolysis. Again it was found that this method of introducing the carboxyl group was largely spoilt by the formation of a great deal of unsaturated material (in this case α-campholytic acid). Nevertheless they were able to isolate a small quantity of a crystalline substance having properties identical with those of inactive camphoric acid. The amount obtained was, however, insufficient for the comparatively exacting analyses of those times. With characteristic generosity they conclude, " The method of formation . . . and the properties leave scarcely room for doubt that it was *i*-camphoric acid. . . . In the meantime Komppa has published his brilliant synthesis of camphoric acid, which, once for

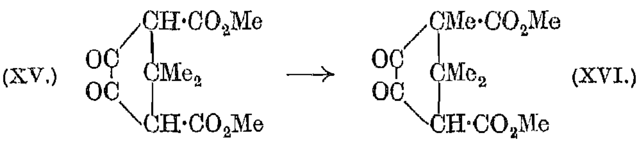
all, establishes the correctness of Bredt's formula, and it is therefore quite unnecessary to investigate our much less satisfactory process any further."



(VII.) (VIII.) (IX.) (X.) (XIV.) (XI.) (XII.) (XIII.)

Nevertheless a few years later a sample of inactive camphoric acid, sent by Noyes, crossed the Atlantic, and Perkin and Thorpe were unable to resist the temptation of finding out whether their synthesis had been successful. The work was repeated and the product was fully identified with Noyes's material. There can therefore be no doubt that Perkin and Thorpe had achieved an independent synthesis of camphoric acid almost simultaneously with that of Komppa.

In 1909 Komppa published the full details of his work and a doubt arose as to its validity. The basis of the Komppa synthesis lay in the methylation of (XV) to (XVI), which was then reduced to camphoric acid :

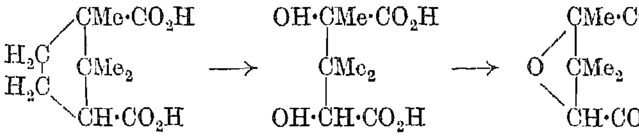


(XV.) (XVI.)

In a joint paper with Blanc, then at the Sorbonne, which was published simultaneously in England (*J.*, 1910, 97, 836) and in France, Komppa's synthesis was questioned on the ground that methylation of (XV) had yielded an *O*-methyl derivative. It was shown that

treatment of the product with alkali led to elimination of the methyl group. Komppa, however, held his ground. He maintained that, whatever occurred during hydrolysis, the methyl group remained intact during the reduction and that the synthetic acid was undoubtedly camphoric and not apocamphoric acid. All doubt was removed when Blanc and Thorpe showed (*J.*, 1911, **99**, 2010) that hydrolysis of (XVI) with very weak alkali yielded a C_8 diketone with the methyl group intact. Their earlier criticism was therefore invalid.

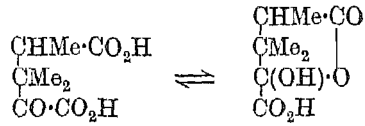
Many years later Thorpe returned to the study of Balbiano's acid, $C_8H_{12}O_5$. To this the discoverer had assigned the formula (XVII), and had interpreted the formation from camphoric acid as follows :



(XVII.)

Thorpe (with Kon and Stevenson, *J.*, 1922, **121**, 650; with Pandya, *J.*, 1923, **123**, 2852; and with Rothstein and Stevenson, *J.*, 1925, **127**, 1072) decided that Balbiano's formula was unacceptable and that the reactions of the acid could only be fully accounted for if it was represented as α-keto-α′ββ-trimethylglutaric acid (XVIII) in tautomeric equilibrium with the hydroxy-lactonic acid (XIX) :

(XVIII.)



(XIX.)

Conclusive evidence in support of this view was provided subsequently by J. C. Bardhan, in Thorpe's laboratory. He was successful in synthesising the keto-acid (XVIII) by an unambiguous method (*J.*, 1928, 2604). The synthetic acid was identical with Balbiano's acid.

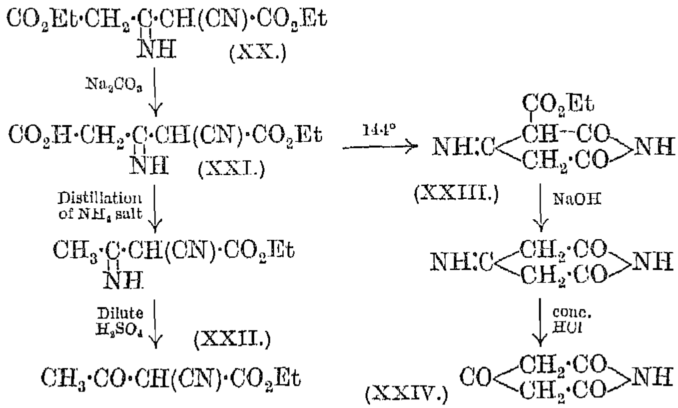
3. *The Formation and Reactions of Imino-compounds.*

Although Thorpe's work on tautomerism and on valency deflection had a greater effect on contemporary chemical thought and aroused greater interest at the time of publication, his fundamental researches on the imino-compounds possibly represent his most permanently valuable contribution to chemical science. He was led to investigate this field in the first place through his interest in ethyl cyanoacetate,

which might well rank as his favourite compound. In 1904, with Baron and Remfry (*J.*, 85, 1726), he discovered that this substance condensed with its own sodio-compound in the following way:

$$CO_2Et{\cdot}CH_2{\cdot}CN + CHNa(CN){\cdot}CO_2Et \longrightarrow CO_2Et{\cdot}CH_2{\cdot}\underset{\substack{\|\\ NH}}{C}{\cdot}CNa(CN){\cdot}CO_2Et$$

(This scheme represents a slight later revision of that originally proposed.) From the product, acid liberated the free β-imino-α-cyanoglutaric ester (XX), the structure of which was shown by its degradation to the known α-cyanoacetoacetic ester (XXII) through the stages shown:

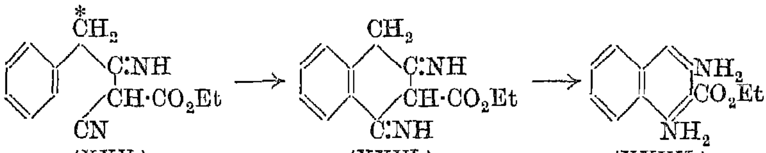


The intermediate acid (XXI) was decarboxylated at 160°, but at a few degrees above the melting point it was cyclised to ethyl glutazinecarboxylate (XXIII), which could be hydrolysed to 2 : 4 : 6-triketopiperidine (XXIV).

These results were of great interest both from the character and reactivity of the products formed and from the novelty of the initial condensation. Thorpe promptly began to investigate the generality of the addition of sodiocyanoacetic ester to the cyano-group. In 1906, with Atkinson (*J.*, 89, 1906), he showed that the sodio-ester condensed with phenylacetonitrile to yield the additive compound (XXV). The structure of this was shown by its fission by means of alcoholic potash into phenylacetic and malonic acids. The sodium compound of (XXV) was methylated * at the starred carbon, for

* The methylation of β-imino-α-cyanoglutaric ester (XX) was fully studied some years later (with Campbell, *J.*, 1910, **97**, 1299).

the methylated product was hydrolysed to α-phenylpropionic acid and malonic acid. Treatment of these substances with cold concentrated sulphuric acid produced a remarkable result; in the space of one minute, the following changes occurred:



(XXV.) (XXVI.) (XXVII.)

The ethyl 1 : 3-naphthylenediamine-2-carboxylate (XXVII) separated as a sulphate when the product was poured on ice. The free base was yellow and the salts were colourless, suggesting that they had the imino (XXVI) and the amino (XXVII) structure, respectively. The *diamino-ester* on hydrolysis yielded the corresponding acid, which above the melting point yielded 1 : 3-naphthylenediamine, identical with that obtained from 1 : 3-dinitronaphthalene. It was found, moreover, that ethyl sodiocyanoacetate was not an essential component in the initial condensation because phenylacetonitrile condensed with itself in the presence of sodium ethoxide to yield successively the compounds (XXVIII) and (XXIX) together with some cyanobenzyline (trimeride).

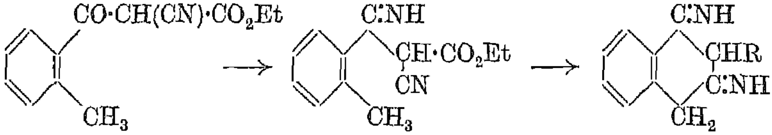
$$\underset{\text{(XXVIII.)}}{Ph{\cdot}CH_2{\cdot}\underset{\parallel}{\overset{}{C}}{\cdot}CHPh{\cdot}CN \atop NH} \qquad \underset{\text{(XXIX.)}}{Ph{\cdot}CH_2{\cdot}CO{\cdot}CHPh{\cdot}CN}$$

The imino-nitrile (XXVIII) was cyclised by sulphuric acid to 2-phenyl-1 : 3-naphthylenediamine, a compound which was subsequently examined in detail (Lees and Thorpe, *J.*, 1907, **91**, 1282).

In 1907, with Atkinson and Ingham, Thorpe showed the reaction to be even more general, because benzonitrile condensed readily with ethyl sodiocyanoacetate. It was therefore clear that, of the two nitriles taking part in the Thorpe reaction (as it came to be called), only one needed to be able to form a sodium derivative.

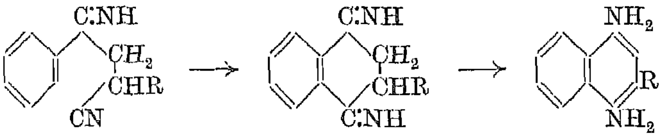
o-Toluonitrile exhibited steric hindrance towards the reaction, the yield being low, but the product (XXXI) could be made by fusing the corresponding keto-ester (XXX) with ammonium acetate. It was found that the *o*-methyl group of (XXXI) was remarkably reactive, the compound being quantitatively cyclised by cold sulphuric acid to the corresponding naphthylenediamine derivative (XXXII, $R = CO_2Et$.)

A similar series of reactions was performed by condensing *o*-toluonitrile with phenylacetonitrile, the final product having the structure



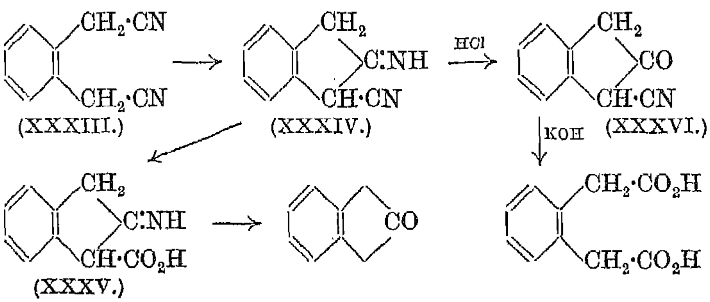
(XXX.) (XXXI.) (XXXII.)

(XXXII, R = Ph). It was found that there was no tendency for the formation of a di-iminohydrindene ring under the same conditons, but Thorpe (*J.*, 1907, **91**, 1004) was able to prepare derivatives of 1 : 4-naphthylenediamine by a similar cyclisation :



Another paper with Atkinson (*ibid.*, p. 1687) describes similar condensations and cyclisations in which the starting materials were cyanoacetic ester and the three tolylacetonitriles. Thorpe found, however, that ethyl α-cyano-γ-phenylacetoacetate, that is, the ketone corresponding to the imine (XXV), did not cyclise to the isomeric aminonaphthol derivative (*J.*, 1907, **91**, 1899).

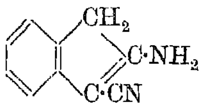
An important advance was made in the following year when the first intramolecular reaction involving two nitrile groups was discovered (Moore and Thorpe, *J.*, 1908, **93**, 165). A trace of sodium ethoxide was found to convert the dinitrile (XXXIII) into β-imino-α-cyanohydrindene (XXXIV). The structure of the product was proved by the reactions shown below :



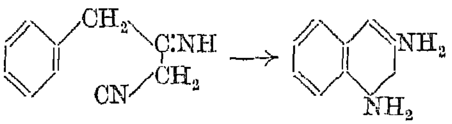
(XXXIII.) (XXXIV.) (XXXVI.) (XXXV.)

This work raised afresh the question of fine structure. Were the compounds better represented as imines or as amines? For example, was the original condensation product (XXXIV) or (XXXVII)? These questions could be answered with certainty in the case of most of the products. For instance, the original product was undoubtedly the imine (XXXIV) because of its ease of hydrolysis and lack of salt-forming properties. On the other hand, the acid (XXXV) and its derivatives behaved as amines (formulæ corresponding to XXXVII). The acid yielded a hydrochloride and lost carbon dioxide more readily than ammonia. α-Cyanohydrindone (XXXVI) also exhibited tautomeric properties, in this case of the keto-enol type. The substance yielded *O*-ethers from the enolic form and carbonyl derivatives from the keto-form.

Thorpe's next collaborator in this field was S. R. Best, and in 1909 the two published four important papers (*J.*, **95**, 8, 261, 685, 1506). In the first it was shown that for the ring closure of β-imino-γ-phenylbutyronitrile (XXXVIII) to 1 : 3-naphthylenediamine (XXXIX) the α-substituents (phenyl, carbethoxyl) which had been present in



(XXXVII.)



(XXXVIII.) (XXXIX.)

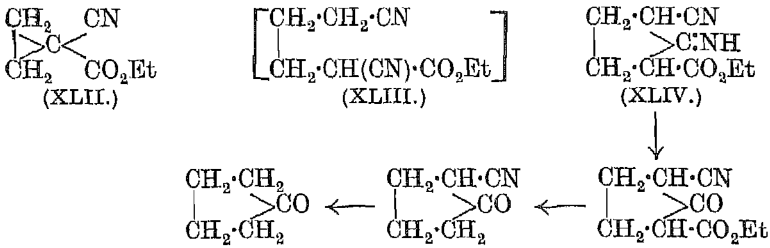
previous compounds were unnecessary. The ring closure proceeded smoothly in cold concentrated sulphuric acid. Following this the auto-condensation of the three tolylacetonitriles was studied.

An important research on the extension of the reaction to the aliphatic field followed. Thorpe showed (*J.*, 1909, **95**, 1901) that adiponitrile (XL) was cyclised to imino-2-cyano*cyclo*pentanone (XLI) when it was warmed with sodium ethoxide :

$$\text{(XL.)}\quad \begin{array}{l} CH_2{\cdot}CH_2{\cdot}CN \\ | \\ CH_2{\cdot}CH_2{\cdot}CN \end{array} \longrightarrow \begin{array}{l} CH_2{\cdot}CH_2 \\ |\qquad\ \ \ >C{:}NH \\ CH_2{\cdot}CH{\cdot}CN \end{array}\quad \text{(XLI.)}$$

This represents the reaction stripped to its essentials. Best and Thorpe were able to show that the same process occurred in a slightly more complicated case. Carpenter and Perkin, by the action of ethyl sodiocyanoacetate on ethylene dibromide, had obtained *cyclo*propanecyanoacetic ester (XLII), together with a compound formed by reaction with a second molecule of the cyano-ester, and believed to be (XLIII). Best and Thorpe showed that this, too,

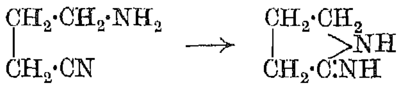
was a *cyclo*pentane derivative (XLIV), and could be hydrolysed in the stages shown:



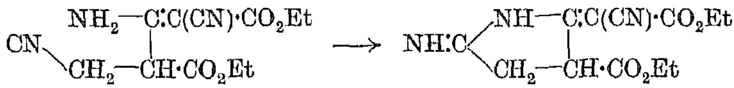
(XLII.) (XLIII.) (XLIV.)

An important distinction was noticed between the ketones, which were stable to acids but suffered ring-fission with alkalis, and the imino-compound, which was stable to alkali but lost ammonia on treatment with acids.

They next examined the possibility of forming heterocyclic compounds from amino-nitriles, *e.g.*,



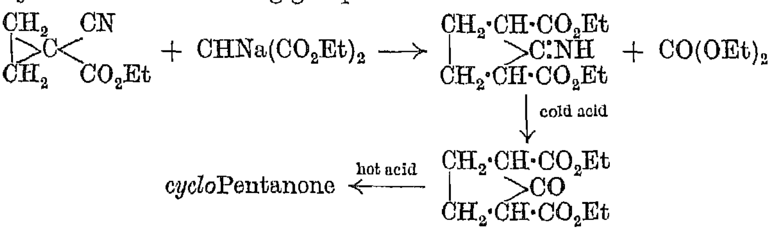
It was found that the amino-nitrile (XLV) could be cyclised to the pyrrolidine derivative (XLVI):



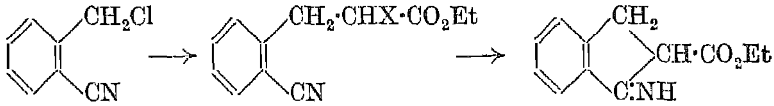
(XLV.) (XLVI.)

A remarkable series of transformations was observed when the product was treated by mild reagents. The chemistry of the substances in this group is much complicated by the ease of imino-amino tautomerism.

A. D. Mitchell and Thorpe (*J.*, 1910, 97, 997) next showed that for the intramolecular formation of a *cyclo*pentanone-imine only one cyano-group was essential, and the place of the second could be taken by some other activating group. Thus:

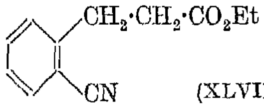


This established a close connection between the Thorpe and the Dieckmann condensation. It was shown (*ibid.*, p. 2261) that a similar cyclisation of a monocyano-compound, accompanied by loss of a carbethoxyl group as ethyl carbonate, also occurred in the condensations first studied by Gabriel and Hausmann. Thus the product of the interaction of *o*-cyanobenzyl chloride and a sodio-ester $CHNa(X){\cdot}CO_2Et$ was proved to have the formula (XLVII) and not that (XLVIII) proposed by the discoverers.



(X = CO_2Et, $CO{\cdot}CH_3$) (XLVII.)

Thorpe's interest in imino-compounds soon attracted him to the neglected reaction of Guareschi. In later years, with Kon (*J.*, 1919,



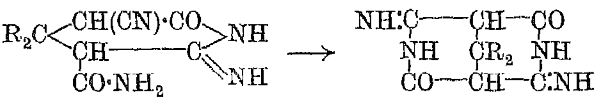
(XLVIII.)

115, 686; 1922, **121**, 1765), he did much to improve and popularise this. It consists in the condensation of a ketone with cyanoacetic ester and ammonia and leads to the precipitation of the " Guareschi imide " (XLIX) as the ammonium salt :

$$R_2CO + \begin{matrix} CH_2(CN){\cdot}CO_2Et \\ CH_2(CN){\cdot}CO_2Et \end{matrix} + NH_3 \longrightarrow R_2C\!<\!\begin{matrix} CH(CN){\cdot}CO \\ CH(CN){\cdot}CO \end{matrix}\!>\!NH$$

(XLIX.)

Hydrolysis of these imides with sulphuric acid gives excellent yields of ββ-dialkylglutaric acids, and the process constitutes perhaps the best existing preparative method for these substances. Thorpe's earliest experiences with the method were not very encouraging, and he therefore (with Thole, *J.*, 1911, **99**, 422) devised a modification. Cyanoacetamide in water containing a little piperidine or alkali was found to condense with ketones to yield crystalline precipitates. The main products, however, were not symmetrical like the Guareschi imides, but were of the structural type (L) :



(L.) (LI.)

Nevertheless a small amount of the corresponding Guareschi imide was formed as a by-product (Thorpe and Wood, *J.*, 1913, **103**, 1569; Kon and Thorpe, *J.*, 1919, **115**, 686). The unsymmetrical cyano-amides, such as (L), were able to cyclise further to the bridged di-imino-di-imides (LI).

The Guareschi reaction is not suitable for the preparation of β-monosubstituted glutaric acids from aldehydes, because the condensation products are stable pyridine compounds. The cyano-acetamide method, however, goes very well, to give the open-chain dicyanoglutaramides, which are smoothly hydrolysed to the corresponding acids (Day and Thorpe, *J.*, 1920, **117**, 1465):

$$R{\cdot}CHO \longrightarrow R{\cdot}CH\begin{matrix}\diagup CH(CN){\cdot}CO{\cdot}NH_2\\ \diagdown CH(CN){\cdot}CO{\cdot}NH_2\end{matrix} \longrightarrow R{\cdot}CH\begin{matrix}\diagup CH_2{\cdot}CO_2H\\ \diagdown CH_2{\cdot}CO_2H\end{matrix}$$

4. *Glutaconic Acids.*

Thorpe became interested in these substances at the time of his synthetic work with Perkin and remained actively concerned with their investigation for a quarter of a century. The chemistry of these substances is very complicated. There is an intricate interplay of stereochemical inversion and tautomeric change. We know to-day that the special hypothesis advanced by Thorpe to explain their behaviour is no longer valid. Nevertheless it is due to the stimulus given by his work in the field that the truth has finally come to light, mainly through the work of Kon and of Packer, both members of Thorpe's school.

Thorpe's cardinal point of view is well stated in a paper in 1923 (*J.*, **123**, 3343). "All experiments on the glutaconic acids . . . combine to show that there is something in the constitution of these substances which conventional symbols do not explain, and that this 'something' is connected with the mobile hydrogen atom of the system, because it disappears when that atom is absent; we assume, therefore, that this structural peculiarity is connected with the mode of attachment of the mobile hydrogen atom to the rest of the molecule."

It will be convenient at this point to summarise the abnormalities in glutaconic acid chemistry which led Thorpe to take up this position. They are:

(i) The apparent equivalence of the α- and the γ-position.
(ii) The absence of the full number of geometrical isomerides.

(iii) The apparent impossibility of obtaining optically active compounds.
(iv) The abnormal reactivity in additions.
(v) The peculiarities of anhydride formation.

It was the first two of these considerations which led to Thorpe's initial dissatisfaction with the conventional formula

$$\underset{\alpha}{CO_2H \cdot CH}\text{:}\underset{\beta}{CH}\cdot\underset{\gamma}{CH_2}\cdot CO_2H.$$

The system of graphic formulæ due to the genius of Frankland, Couper, and others has been the mainstay of organic chemistry. It nevertheless, like all systems, has its disadvantages, and one of these is its lack of ability to suggest abnormal reactivity. This shortcoming exercised the minds of many chemists at the beginning of the century. It was a time when the conception of valency lacked the comparative precision which it has acquired to-day and when men of bold minds were able to express themselves with freedom. The shadow of the physicist had yet to fall upon the landscape, and organic chemists were still living in a happy Arcadian simplicity. There arose the "centric" formula for benzene, the partial valencies of Thiele, and, in 1905, Thorpe's "normal" formula for glutaconic acid : $CO_2H \cdot \dot{C}H \cdot CH_2 \cdot \dot{C}H \cdot CO_2H$. It was held that this best represented the structure of the ordinary crystalline acid. It indicated a resemblance to the aromatic type, a diminution of unsaturated reactivity, and explained the equivalence of the α- and the γ-position and the absence (at that time) of a second geometrical isomeride. As the facts stood in 1905, the "normal" formula was a better *reaction* formula than the conventional. It was, however, too adventurous to receive general acceptance, and was in particular the target for criticism by Feist. A long controversy ensued, singularly lacking in acrimony. It now appears that, although the "normal" form has outlived its usefulness, Feist tended to under-estimate the possibilities of double-bond migration in glutaconic acids and to over-emphasise the importance of a purely stereochemical inversion in explaining the various phenomena.

In 1911, with Thole, Thorpe returned to the study of the apparent equivalence of the α- and the γ-position, and examined the peculiar tendency of glutaconic acids to yield chloro- and hydroxy-anhydrides on treatment with acetyl chloride. This work was extended to other members of the glutaconic series and to the aconitic acids in 1912 (with Bland). It was emphasised that in unsymmetrically

substituted molecules the tendency for the acid (or its derivatives) to exist in a conventionally double-bonded (labile) form was increased. Later, with Wood, the alkylation of glutaconic ester was studied. It was shown that the results obtained by alkylating the pure sodio-derivative in dry ether with methyl iodide differed from those obtained by the use of sodium ethoxide. The former led to successive α- and γ-methylations, and the product was then capable of a final alkylation to an $\alpha\alpha\gamma$-trimethylglutaconic ester. In sodium ethoxide, however, both methyl groups entered the α-position, the system lost its mobile hydrogen atom, and was incapable of further alkylation. These results were correlated with the positions taken up by the double bond at the various stages.

In 1919 Thorpe (*J.*, **115**, 679) extended some earlier observations on the additive reactions of glutaconic derivatives. He pointed out that, in general, the "normal" compounds do not form additive compounds readily, whereas the labile compounds exhibit the ordinary reactions of the double bond. He observed, however, that "normal" β-methylglutaconic ester reacted with sodiocyanoacetic ester to give, in low yield, a condensation product, which was hydrolysed to γ-methylbutane-$\alpha\beta\delta$-tricarboxylic acid. The formation of this was attributed to 1 : 3-addition to the free valencies of the normal form. The possibility of such addition was elaborated in subsequent papers with Ingold (*J.*, 1921, **119**, 492) and with Ingold and Oliver (*J.*, 1924, **125**, 2128). The second of these papers illustrated the important point that, when additive reactions did occur to the "normal" form, the products very readily "reverted to type", *i.e.*, they tended to re-acquire the stable "normal" glutaconic arrangement. In the present state of our knowledge it is preferable to attribute the anomalous 1 : 3-reactions to reversed 1 : 2-additions to $\alpha\beta$-double-bonded forms.

The main interest in the field then shifted to a cyclic acid of the glutaconic type, 3-methyl*cyclo*propene-1 : 2-dicarboxylic acid, which was investigated by Goss, Ingold, and Thorpe during the years 1923—25, and subsequently by Kon in Thorpe's laboratories.

The rapid increase in the knowledge of three-carbon tautomerism during the nineteen-twenties led to the development of improved techniques, and the time became ripe for a reinvestigation of the many puzzling features of glutaconic acid chemistry. This was carried out in Thorpe's laboratories during 1930—33, and led to a general reinterpretation on the basis of three-carbon tautomerism and *cis–trans* isomerism. The death-blow was simultaneously

given to the " normal " form by Packer and Thorpe (see *J.*, 1926, 1199; 1931, 547; 1934, 1653), who resolved " normal " $\alpha\gamma$-dimethylglutaconic acid into optically active forms by means of its acid strychnine salt. It was a fitting tribute to Thorpe's scientific integrity that he should at the end assist in the destruction of a theory which he had defended with so much skill and determination.

5. *Tautomerism and Bridged Rings.*

After Thorpe's translation from Sheffield to the Imperial College his work becomes more varied and it is correspondingly more difficult to classify and review it.

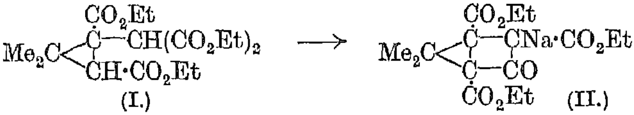
Ever since his earlier investigations on cyanoacetic ester, glutaconic acids, and imino-compounds, Thorpe was keenly alive to the widespread occurrence of tautomeric change in organic compounds. He did as much as anyone in this country to propagate the idea of the shifting double bond and the mobile hydrogen atom, and he played an important part in laying the foundation on which our modern conceptions of tautomeric change are based. In 1922 (*J.*, **121**, 650) he advanced what is perhaps the best and most logical definition of tautomerism which we have. " The word tautomerism is used to denote reversible isomeric change, such change being brought about in solution, or in the liquid state with or without the aid of catalysts, to form equilibrium mixtures of the individuals showing tautomerism."

One of Thorpe's most important contributions to the subject was made in 1911. With Thole (*J.*, **99**, 2182) he observed that, when the last mobile hydrogen atom in a tautomeric system was replaced by alkyl, then " . . . the tendency for the compound to acquire that hydrogen atom which is necessary to enable it to react in its tautomeric form is such that any group capable of replacement by hydrogen is at once eliminated in the presence of a suitable reagent ". Thus an alkylated carbethoxyglutaconic ester would react with sodium ethoxide with the elimination of ethyl carbonate :

$$CO_2Et{\cdot}CR{:}CR'{\cdot}CR''(CO_2Et)_2 + NaOEt \longrightarrow CO_2Et{\cdot}CR{:}CR'{\cdot}CNaR''{\cdot}CO_2Et + CO(OEt)_2$$

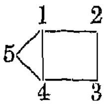
It was shown that this was only a property of unsaturated and potentially mobile systems, saturated malonic esters being unaffected. The theme was further developed for indene derivatives with Ingold (*J.*, 1919, **115**, 143). It was of the greatest importance in Thorpe's general work on imino-compounds and glutaconic acids.

Some of Thorpe's most intricate work was on the tautomerism of bridged ring compounds. His interest in this field had been aroused during some early experiments with Perkin (*J.*, 1901, 79, 729). They had condensed αα′-dibromo-ββ-dimethylglutaric ester and sodiomalonic ester, to yield the *cyclo*propane derivative (I). This, when heated with sodium or sodium ethoxide, gave a yellow, stable sodium compound (II) :

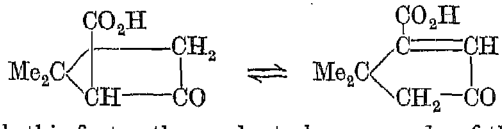


(I.) (II.)

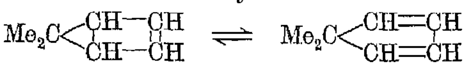
The investigations of the involved and often ambiguous degradation reactions of this bridged-ring compound occupied four years and left Perkin and Thorpe not entirely satisfied with the results. Thorpe returned to the study of these compounds in 1919 with Ingold (*J.*, **115**, 320). They undertook a detailed comparison of the behaviour of substances of type (II) with that of the corresponding compounds with a *cyclo*hexane ring in place of the *gem*-dimethyl group. The research was centred around (i) a comparison of the ease of closure of the *cyclo*butane ring (3 : 4-bond formation), (ii) hydrolytic fission of the *cyclo*propane ring (4 : 5-bond fission), (iii) hydrolytic decomposition of the methylation products of the bridged compounds (stability of 4 : 5 and 2 : 3 bonds), and (iv) fission of the bridge (1 : 4) by reduction.



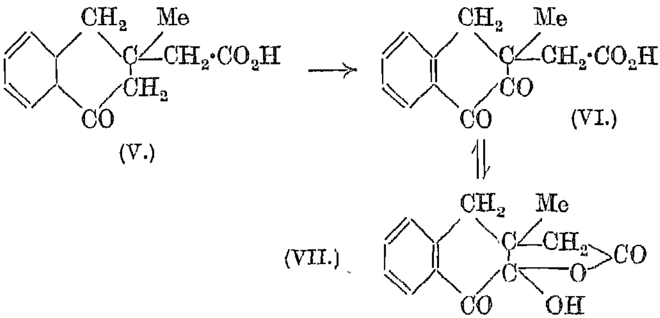
In 1922, a further investigation of compounds of this type was made (Farmer, Ingold, and Thorpe, *J.*, **121**, 128), particularly of the keto-acid (III). The conclusion was reached that this substance was capable of reacting in a monocyclic unsaturated form (IV). For this phenomenon the convenient term " intra-annular tautomerism " was coined.

(III.)  (IV.)

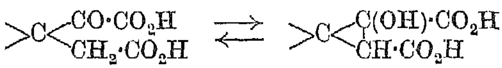
To establish this fact a thorough study was made of the oxidation with potassium ferricyanide and permanganate and of the reactions with chlorine, bromine, and nitrosyl chloride. A year later, a study was made by Thorpe, Ingold, and their collaborators of the related intra-annular tautomeric system :



Contemporaneously, Thorpe was studying the keto-enol tautomerism which can occur between a ring compound and its open-chain isomeride. This is now recognised to be of widespread importance, and Thorpe's term "ring-chain tautomerism" is in general use. The compound initially studied, with Kon and Stevenson, was the intermediate oxidation product of the acid (V). This was found to be capable of reacting either in the keto- (VI) or the hydroxy-lactone (VII) form :



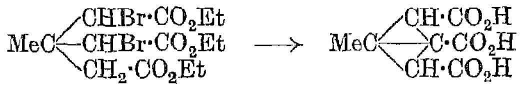
The substance behaved as an α-diketone in yielding a quinoxaline derivative, and as a lactol in giving an acetyl compound. Moreover, it was observed that the solution in water or alcohol, initially colourless, became yellow when warmed, the colour change being reversible. This was interpreted as the reversible formation of the diketone (VI) from its tautomeride. Another example of ring-chain tautomerism was seen in Balbiano's acid, which has already been mentioned. Still another came from the related study of α-ketoglutaric acids containing various β-substituents.



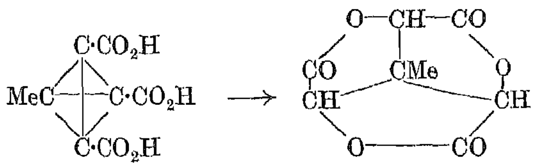
This will be more appropriately considered later, in connection with valency deflection. The conception of ring-chain tautomerism was used to interpret the colour reactions of the fluoresceins and rhodamines (Dutt and Thorpe, *J.*, 1924, **125**, 2524). It was also the theoretical basis of an excursion made by Thorpe with Ingold and J. W. Baker into sugar chemistry. A study of the velocity of the mutarotation of tetra-acetyl *d*-glucose in dry and in moist ethyl acetate led to the view that the reaction was a pure example of ring-

chain tautomerism and did not involve the intermediate formation of a hydrate (*J.*, 1924, **125**, 268).

Thorpe was perennially interested in complex carbon-ring structures. The most unusual with which he worked was described in a paper with Beesley (*J.*, 1920, **117**, 598) after earlier preliminary work. It was found that the bromination of ββ-dimethylpropane-tricarboxylic acid gave the dibromo-ester (VIII). When this was treated with aqueous potash at a high temperature (" as quickly as possible, consistent with safety ", as Thorpe's phrase runs), it yielded the bridged *cyclo*butane acid (XI) :

(VIII.)  (IX.)

This acid was isolated in three forms, two of which gave anhydro-acids. The acids were stable to boiling acid and alkali, and did not react with bromine or permanganate. One of them, on treatment with bromine and phosphorus pentabromide, and subsequently with alcohol, gave a bromine-free product, which on hydrolysis yielded a tribasic acid, $C_8H_6O_6$. This remarkable substance appears to have the structure (X), the four cyclic carbon atoms being situated at the corners of a tetrahedron. In support of this the substance yields no anhydride, has no reaction with bromine, and does not

(X.)  (XI.)

reduce permanganate in the cold. It is oxidised by hot permanganate to methylsuccinic acid and converted by hydrochloric acid under pressure into the trilactone (XI).

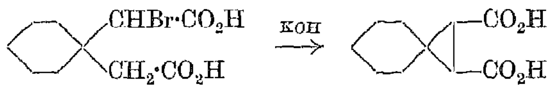
6. *Valency Deflection.*

The developments in this field are associated jointly with the names of Thorpe and Ingold. Their collaboration began in 1914 and lasted until 1928.

The point of departure in their work was the realisation that the regular tetrahedron was an inadequate general representation of the carbon atom. They were the first to give definite expression to the

view that the angles between the valencies of a carbon atom could be modified by substitution. This fruitful idea marked a great advance. It at once permitted a correlation of a large number of observed facts in which highly substituted molecules behaved in a different manner from their unsubstituted analogues. This central conception has been abundantly verified by exact physical measurements of recent years. We may mention Debye's classical *X*-ray investigation of the chlorinated methanes, in which it was shown that the carbon–chlorine distances remained constant throughout the series, but the chlorine–chlorine distance altered owing to a change in the inter-valency angle. The angle between the $C{<}^{Cl}_{Cl}$ valencies is calculated to rise from 116·4° in chloroform to 123·8° in methylene chloride.

Thorpe and Ingold's first paper in this field (with Beesley, *J.*, 1915, **107**, 1080) was concerned with the investigation of the effect produced by the alteration of the tetrahedral angle owing to ring formation on the formation of and stability of a second ring joined to the first by a common quaternary carbon atom. It was considered that a bending outwards of the valencies in the original ring would cause the other valencies to distribute themselves equally in the remaining space. They would come closer together than the usual 109° 28′, and hence there would be a greater facility for the formation of a second ring. The reaction chosen for investigation was the form-

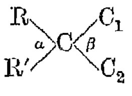


(XIII, as half ester.) (XII.)

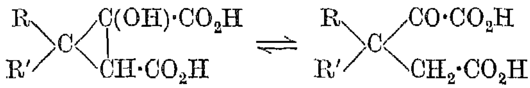
ation of the *spiro*-compound (XII) from a monobrominated derivative of *cyclo*hexane-1 : 1-diacetic acid (XIII). The formation of bromo-lactones from the corresponding dibromo-esters was also examined.

It was unfortunate that a *cyclo*hexane derivative was used in this early work. At the time it was almost universally believed that this ring was " strained " in the Baeyer sense, that it was uniplanar and had an internal angle of 120°. We now know that the *cyclo*hexane ring can adopt multiplanar forms, although these are not sufficiently permanent to lead to isolable isomerides unless stabilised by fusion with another ring. It is impossible as yet to draw any final conclusion as to the size of the internal angle in *cyclo*hexane, but most chemists now regard this as being approximately tetrahedral and the ring as being either largely or entirely free from strain.

In 1921 Ingold extended the original conception to acyclic compounds. For assessing the value of the angle α between two substituent groups R,R′ a calculation based on the molecular volumes of the groups was used. As in the early work in which R,R′ were part of a ring, the value of the emergent angle β was calculated. This provided a theoretical basis for a study of the effect of substituents on the relative ease of ring formation involving the atoms C_1, C_2 and on the stability of the rings so formed.



On this basis a series of investigations was instituted over a period of years. The main reactions studied were (i) the ease of formation of *cyclo*propane compounds such as (XII); (ii) the stability of these acids (caronic acid type) towards fission by hydrochloric acid; (iii) the ring-chain tautomerism between the hydroxy- and keto-acids of types (XIV) and (XV) in concentrated aqueous alkali :

(XIV.)  (XV.)

One of the most interesting observations was the general agreement in behaviour between the *gem*-dimethyl compounds and their *cyclo*pentane analogues, as predicted by the theory. The results of the study of the ring-chain tautomerism (XIV $\rightleftharpoons$ XV) were perhaps the most striking, the following figures being obtained :

	% at equilibrium.			% at equilibrium.	
RR′.	Keto acid.	Hydroxy-acid.	RR′.	Keto-acid.	Hydroxy-acid.
H, H	100	0	Et, Et	38	62
Me, Me	100	0	Pr^a, Pr^a	29	71
*cyclo*Pentane	100	0	*cyclo*Hexane	0	100
Me, Et	100	0			

It was pointed out that these differences are those expected if the substituents produce successive contractions in the intervalency angle β.

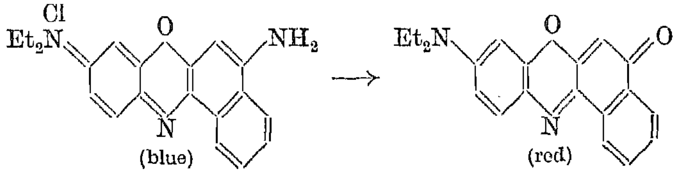
Evidence from another point of view was advanced by Spiers and Thorpe (*J.*, 1925, **127**, 538), who made a study of the dissociation constants of a large number of acids of the succinic and glutaric series. This work was based on the long-recognised conception that the primary and secondary dissociation constants of dicarboxylic acids are largely determined by the distance between the carboxyl groups. The greater the distance, the smaller the primary, and the larger the secondary, dissociation constant. Spiers and Thorpe's measurements of the primary dissociation yielded results in general agree-

ment with the demands of the valency deflection hypothesis. A fuller investigation has since been made by Gane and Ingold. It remains, however, a matter of difficulty to obtain an entirely satisfactory method of calculating the distance between the carboxyl groups from the ratio of the first and the second dissociation constants, and to evaluate the relative importance of valency deflection and variation in the equilibrium configuration in determining this distance.

The hypothesis of valency deflexion was the target for a good deal of criticism, notably from W. Hückel, which led to a general restatement (Ingold and Thorpe, *J.*, 1928, 1318). Thorpe's final summary of his work in the field was given in his Presidential Address in 1931 (*J.*, p. 1020). We are not to-day in a position to say how important a rôle valency deflection plays in organic chemistry. We know without question that valency angles are deflected and we can be reasonably certain that in this way the ease of various reactions is affected. The task of disentangling this effect from the other influences at work is a task for the future. Thorpe's greatest achievement in this field was to release organic chemists from a habit of thought at once over-rigid and over-simplified.

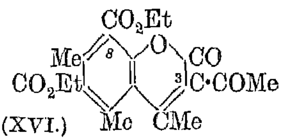
5. *Miscellaneous.*

The wide range of Thorpe's chemical interests is reflected in the number of papers which he published from time to time on miscellaneous matters which caught his attention. The first of these dealing with a subject quite foreign from anything he had previously investigated, was entitled " A reaction of certain colouring matters of the oxazine series " (*J.*, 1907, **91**, 324). This research arose from a histological observation made by Professor Lorrain Smith and Dr. Powell White of Manchester. They had used certain oxazine colours for staining pathological specimens. They found that they not only stained the protein blue but the fat red. Thorpe revealed the underlying chemistry of the process. He showed that the red colour could be reproduced in hydrocarbon solvents and was due to a hydrolysis; for example, in the case of Nile Blue A :

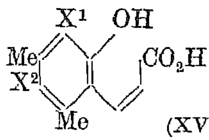


He published another paper with Lorrain Smith on Weigert's method of staining medullated nerve fibres in the following year (*J. Path. Bact.*, 1908, **13**, 14).

Two other interesting papers removed from Thorpe's usual lines of research appeared in 1915. One with Jordan (*J.*, **107**, 387) was on the formation of coumarin derivatives and the preparation of stable coumarinic acids. It was shown that the neutral substance formed by the action of sodium ethoxide on ethyl *iso*hydracetate was the coumarin derivative (XVI):



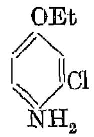
(XVI.)



(XVII.)

It was shown that the acetyl group in position 3 was remarkably stable. So also were the corresponding coumarinic acids (XVII) where $X^1 = CO_2H$ or CO_2Et and $X^2 = CO_2Et$ or H, which resisted cyclisation to the corresponding coumarins. The stability of these acids was due to the CO_2H (or CO_2Et) in position 8. When this was replaced by hydrogen, the lactone ring was easily formed.

The other research arose from the work done at South Kensington during the early months of the war of 1914—18 on the preparation of phenacetin. Thorpe and Miss Hurst (*J.*, 1915, **107**, 934) found that the reduction of *p*-nitrophenetole with tin and concentrated hydrochloric acid gave, not *p*-phenetidine, but the chloro-derivative:



Later Thorpe investigated the formation of derivatives of tetrahydronaphthalene and of indene from γ-phenyl fatty acids (with Stevenson and others, *J.*, 1922—24). The titles given below will convey some idea of the variety of work in other fields:

"The Action of Bromine on β-Hydrindone" (with Creeth, 1908).

"The Replacement of Alkyl Groups in Tertiary Aromatic Bases" (with Wood, 1913).

"Asymmetric Replacement in the Meta-series" (with Gough, 1919).

"The Intermolecular Condensation of Methyl Ethyl Ketone in the Presence of Calcium Carbide" (with Becker, 1922).

"The Influence of Substituents on the Formation and Stability of Hydantoins" (with Ingold and Sako, 1922).

"The Formation of Bromine Derivatives of Carbon Compounds without the Production of Hydrogen Bromide" (with Gupta, 1922).

"The Formation of Stable β-Lactones" (with Bains, 1923).

"The Relative Stability of Open-Chain Dibasic Acids containing Odd–Even Numbers of Carbon Atoms" (with Challenor, 1923).

"The Properties of Conjugated Compounds" (with Farmer and others, 1927—28).

In addition to his original memoirs, Thorpe carried out a large amount of other writing. He undertook the gigantic task of editing with Dr. M. A. Whiteley, the Supplementary and the New Editions of the "Dictionary of Applied Chemistry" founded by his namesake, Sir Edward Thorpe. He also wrote "The Synthetic Dyestuffs" in collaboration with J. C. Cain, and later with R. P. Linstead; "The Vat Dyestuffs" in collaboration with C. K. Ingold; and "A Student's Manual of Organic Chemical Analysis" with M. A. Whiteley. He contributed to the "Annual Reports on the Progress of Chemistry" in 1914 and wrote a section of the Memorial to W. H. Perkin, jun. These make up a volume of achievement which reveals the wide knowledge of the chemist and the unquenchable vitality of the man.

THOMAS MARTIN LOWRY

1874—1936

LOWRY was a Methodist. Born at Low Moor, Bradford, on October 26th, 1874, he was the son of a Methodist minister, the Rev. E. P. Lowry, who was a chaplain at Aldershot for twenty-seven years; and he was named after another Methodist minister, the Rev. Thomas Martin, his great-grandfather. He was educated at Kingswood School, a Methodist foundation, and, later, he taught in a Methodist college, Westminster Training College. He married, in 1904, Eliza Wood, the daughter of a Methodist minister. He became a governor of several Methodist schools and colleges, held various other offices, and was a local preacher in the Methodist Church. In an article in the *Methodist Recorder* shortly before his death in 1936 he wrote: " My own personal religion has been influenced far more by my Methodist ancestry and training than by the profession in which my life has been spent ". When he died on November 2nd, 1936, the memorial service, which was attended by many distinguished scientists and representatives of learned societies, was held in the Methodist Chapel in Cambridge which he had attended faithfully for sixteen years, and his two favourite hymns were sung. It is against this background of Lowry the Methodist that Lowry the Scientist must be seen.

Lowry the Scientist developed at the Central Technical College of the City and Guilds Institute, South Kensington, which he entered in 1893 as holder of a Clothworker's Scholarship. Later, he was assistant to H. E. Armstrong for seventeen years, from 1896 to 1913. The marks of Armstrong's training were left on him as indelibly as on so many of his contemporaries. It was Armstrong who started him on his researches on the stereochemistry of the α-derivatives of camphor, which led him to his classical work on dynamic isomerism; and it was Armstrong who inculcated in him the passion for chemical crystallography which coloured much of his thought and his later teaching.

Lowry began teaching during this period, but apparently had a

T. M. LOWRY

poor opinion of the students—" The noisy engineers to whom I tried to teach Phys. Chem. at S. Kensington " he called them. He became Lecturer in Chemistry at Westminster Training College in 1904, with more success. One of his early pupils at Westminster wrote: " We were often amazed by his marvellous memory, his ingenuity as an experimenter, and his remarkable powers as a teacher and counsellor. He was always ready to help those who sought his advice; and his curious methods of examining us, his boundless energy, and his versatility, were striking features of his personality." At Guy's Hospital, where Lowry was appointed Lecturer in Chemistry in 1912 and where he subsequently became the first Professor of Chemistry in any London Medical School, his influence was not so marked; but it was war-time, and he and his assistants were far too busy investigating the properties of ammonium nitrate and developing amatol to devote much time to the few medical students. It was early in this period (1915) that Lowry published the first of his " teaching " books, the " Historical Introduction to Chemistry ", in which he illustrated the belief, to which he adhered faithfully throughout his life, that a true knowledge of a science can only be acquired when its historical development is understood.

In 1920 a Chair of Physical Chemistry was created in Cambridge with the aid of a benefaction from the Oil Companies, and Lowry was chosen to fill it. Far from bringing relaxation after his labours of the war years, this appointment inaugurated a new burst of strenuous activity, and the last sixteen years of his life were devoted to building up his Department to an eminent position in the chemical world. He was at last able to direct his teaching to the training of advanced students and research workers, a task in which he found much pleasure and to which he devoted considerable care and energy. Books, all examples of clarity and most careful preparation, and all with a definite teaching purpose, appeared at regular intervals, beginning with the " Inorganic Chemistry " in 1922, and ending with what was perhaps his most important contribution to scientific literature, since it is the only standard work in English on the subject, " Optical Rotatory Power ", in 1935. He delighted in the construction of optical apparatus of all kinds, and raised the equipment of this section of the laboratory to a high state of efficiency. Above all, he gathered round him a continuous succession of research workers of all shades of training from the pure organic chemist to the pure physicist; and it was with them as his collaborators that he wrote a steady stream of papers—about three hundred in all—

nearly all of which were marked by zealous insistence on precise experimental data, clear exposition, and logical argument. His technique of writing scientific papers was characteristic. Each was drafted at great speed, and often piecemeal, on loose sheets of paper in pencil. As each section was completed, it was corrected and re-corrected, and then typed. The finished draft was next attacked with scissors and paste, re-arranged, amended, and often torn up and re-started. After much concentrated effort, both by Lowry and his collaborators, the finished draft was put aside " to be slept over ". This process might last until the next morning or for several weeks, or even months, and it often resulted in the draft being destroyed and a completely new paper written; but the finished product was one in which every word had been weighed, all experimental data checked and re-checked, every argument balanced and considered.

Despite the claims of his Department, Lowry did not shirk more public duty. He had acted as Director of Shell Filling from 1917 to 1919; he served on the Trench Warfare Committee and the Chemical Warfare Committee, and he was an Associate Member of the Ordnance Committee at the time of his death. He was an active member of the Faraday Society from the time of its foundation in 1903 and was its President from 1928 to 1930. He served the Chemical Society as a member of the Council from 1912 to 1916 and as Vice-President from 1922 to 1924, and was Vice-President of the Oil and Colour Chemists' Association from 1925 to 1928. In all these offices he strove to bring academic and industrial research into more vital contact. In 1934 he was President of Section B of the British Association; and he took an active part in the work of other scientific bodies and in international conferences. English scientists owe him a debt of gratitude for the efforts he made to obtain the friendship of foreign workers and to bring them as visitors to this country to take part in scientific meetings, such as the Faraday Society Discussions. He delighted to entertain them both in his home and in his laboratory.

Naturally, honours came his way. He was awarded the degree of D.Sc. of London University in 1899, and was elected a Fellow of the Royal Society in 1914. He was an Honorary M.A. of Cambridge University, and received honorary doctorates from the Universities of Dublin and of Brussels. His service during the First World War gained him the C.B.E. and the Italian Order of St. Maurice and St. Lazarus. With P. C. Austin, he was Bakerian lecturer of the Royal

Society in 1921, and he was invited to give special lectures before several foreign societies.

Despite these honours, Lowry retained an unassuming manner and disposition. He was never really at ease in company. His apparent coldness could be disconcerting to those who did not know him well, but it cloaked a loyal friendliness. In all his relationships with his fellow workers, both senior and junior, he displayed an unwavering integrity, and would claim less than his share of any credit. "Whilst I have been able to supply problems for investigation," he wrote of one of his pupils, "he has himself provided solutions which were beyond the range of my own competence." If more than one person asked for his support in applying for the same post, he would give it to one only, and openly explained to the others why he had done so. He was always ready to encourage young men working in fields in which he had any interest, and he took pains to secure for their ideas a publicity which they could not have attained without his assistance. Lowry's conversation was characterised by a brevity which, for those who knew him, could contain a wealth of meaning. His contributions to scientific discussions were marked by a similar conciseness and were sometimes a source of amusement. Thus, during a discussion at a meeting of the Royal Society, Lowry produced from a capacious trouser pocket a model, about eighteen inches long, constructed of wooden balls and metal springs, such as he delighted to use in his research and for lecture demonstrations. Even his pockets were made for serious use, and his jackets concealed one which would accommodate the whole of his quarto-sized loose-leaf lecture note-book. Both with people and with things Lowry showed great patience. To those working with him, or for him, he was never overbearing. If he disagreed with them, he did so in such a way that no resentment could be felt. "I was commenting, not criticising", was a typical remark. He never listened to complaints, for he trusted those about him to do their own work as conscientiously as he did his. He followed the careers of his students, both in Cambridge and afterwards, with an almost fatherly interest.

No personal memoir of Lowry would be complete without reference first to his dogs and secondly to his holiday camp, both of which had the power to make him unbend. He had a succession of canine companions, and it would be difficult to say whether he was more devoted to them than they to him. In his later years his dog Taffy regularly accompanied him to the laboratory in Free School

Lane, and would lie patiently under the Professor's knee-hole desk, whence he would gnaw the shoes of unwary visitors. Occasionally, when Lowry expected to be away from Cambridge for some length of time, the dog would be put in the charge of the laboratory technician. "Where are you going for your holiday?" Lowry asked this assistant one summer evening. "On a farm, sir." "Taffy will like that," was the reply, and there the matter was closed. For many years the Lowry family went into camp near Ruan Minor, in his ancestral Cornwall, and the fortunate visitor was then privileged to see him, free from the cares of his laboratory, taking his full share in the work and pleasure of the party. It was during these vacations that he found time to preach the Gospel, in the same direct way in which he taught Chemistry, in the little village Methodist chapels of Cornwall, just as he preached, less frequently but with the same satisfaction to both preacher and hearer, in the chapels of Cambridge and of Cambridgeshire.

Lowry gained scientific eminence as a physical chemist, and for the last twenty years of his life held one of the senior professorships of physical chemistry in England; but at the outset of his scientific career he was an experimental organic chemist busily engaged in elementary teaching. His early work in both these directions deeply influenced his outlook throughout his whole life, for his approach to physical chemistry was always that of the experimenter rather than that of the theorist, possibly because his mathematical knowledge was limited, though in this direction he was enthusiastic in stimulating the efforts of collaborators. Lowry's training as an organic chemist made him meticulous in insisting upon the very careful purification of all the substances with which he dealt. Indeed, it can be said that his most significant practical discovery—the demonstration that tautomeric change was seldom spontaneous but needed recognisable catalysts—might never have been made if he had not paid particular attention to the purity of the reagents and solvents which he was using.

Again, Lowry was the writer of a number of elementary text-books of chemistry. This occupation was not pursued solely for the monetary gain, but was part of his general aim to propound logical explanations of scientific facts which would clarify the approach to further discoveries concerning the structure, properties, or reactions of chemical compounds. His books supplemented his constant attempts to drive home in lectures the importance of

fundamental concepts, such as the electronic theory of Langmuir and G. N. Lewis, and he stoutly maintained that chemistry should be taught, even to elementary students, as a virile growing science and not presented as a collected mass of facts. This outlook is probably revealed at its best in his "Historical Introduction to Chemistry", in which he showed clearly how Lavoisier, Cannizzaro and Kekulé successively simplified the whole subject of chemistry by formulating simple generalisations. Lowry took pains to teach the general, rather than the particular, merits of the concepts of Werner, Lapworth, Langmuir and Lewis. Had he lived a little longer he would have expounded the theory of resonance with the same enthusiasm, for his own term "Electromerism" for explaining the symmetry of benzene, carboxylate anions, etc., involved the recognition that many substances existed in stable electronic states which could not be represented completely by Kekulé formulæ. There can be no doubt that in many of these ways Lowry's scientific outlook was derived from his association with his great first teacher—H. E. Armstrong. Unlike Armstrong, however, Lowry, though an eager frequenter of, and a regular speaker at, scientific meetings, was not essentially a controversialist, but strove always to reconcile discrepancies between rival theorists, and to produce a definition or description in terms which revealed the common basis of the topics in dispute.

If ever any man's scientific outlook has been coloured by his religious beliefs, it is true to say of Lowry that his conviction of the necessity of expounding publicly Christian faith and ideals in their simplest form extended to his work as a teacher and as an investigator of chemistry; for, once he had a new fact or a new generalisation to disclose, he did not hesitate to drive it home in simple language, as would a preacher, though never was this done with the object of gaining mere personal credit. One can look on Lowry now as an exponent of the value of the electronic theory of valency who contributed a great deal to achieving the pre-eminence of English-speaking chemists in studies of electronic structures and of the mechanisms of reactions of simple organic molecules. Lowry's personal contribution to the electronic theory was but slight, but as a writer he has undoubtedly influenced most chemists of the present generation.

Lowry's fundamentally simple outlook on chemistry naturally had its failings. Whilst his lectures were of immense value to students, they left untouched many of the more complex and mathematical

aspects of physical chemistry. In the same way, his publications dealing with reaction mechanisms must now be regarded as of qualitative value only. This subject has, in more recent years, developed greatly by mathematical applications of thermodynamics and reaction kinetics, although as a consequence the pictorial simplicity of the subject has become blurred to an extent that Lowry would have deprecated.

Like every experimental organic chemist, Lowry always doubted the wisdom of applying involved mathematics to complex reaction systems having many potentially variable components, particularly since he had himself demonstrated the rôle of trace impurities as catalysts. Nevertheless, when examining a more purely physical topic—the study of optical rotatory power—which was his second main interest for over forty years, he was by no means content with the qualitative explanations of the nineteenth-century stereochemists, such as van 't Hoff, but insisted that any true theory of optical activity must be both quantitative and applicable to radiations of all wave-lengths. He therefore undertook the immense experimental task of studying comprehensively the optical properties of carefully purified substances, and of reducing an enormous amount of experimental data to concise mathematical terms, before attempting to develop a generalised theory. This work was too much for him to complete, but the final volume on "Optical Rotatory Power" does demonstrate the great extent to which he did achieve his initial aims.

An enthusiast always, Lowry was never content with any of his publications, but continually attempted to revise his books, or to add extended notes on his papers, so as to clarify and generalise still further his accounts of theories, with the inevitable result that he died overwhelmed with work, before the normal age for retirement from active academic life. Both the writers of this memoir have been deeply conscious of the extent to which this continual striving for perfection delayed the publication of his books, even though he understood well enough that every scientific work is so irrevocably dated that it can never do more than bring up to an arbitrary limit the historical account of the subject with which it deals. Nevertheless he planned them so that supplementary chapters could be added to deal with future developments of the subject.

Only those who worked in intimate association with him can appreciate Lowry's enthusiasm for fine experimental work, and his keen interest in apparatus. His first thermostat, without which

none of his earlier work could have been performed adequately and of which a model was placed in the Science Museum, his spectro-polarimeter with its double monochromatic devices, and his method for producing intense cadmium arc spectra, testify to his experimental skill. His demonstrations of these, and of the 48-cm. quartz column, cut in sections from a single crystal, with which the classical measurements of rotatory power were made, gave pleasure to countless visitors.

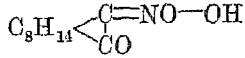
Lowry's research interests were inherently so simple that they have not inspired many of his students to continue to work in precisely the same field, but on comparing present trends with those of 1936 it is astonishing to see the extent to which the concepts which he taught have developed. These recent advances have been in the main due to the contributions of more purely "physical" chemists, or even of mathematical physicists, and the place that Lowry held as a harmoniser of the concepts of the organic and the physical chemists has not yet been so adequately filled by any successor.

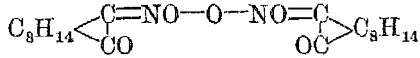
His Work: I. The Mechanism of Chemical Change.

Lowry's first research was an investigation of the stereochemistry of the α-substituted derivatives of camphor. He showed that the chlorination of α-bromocamphor and the bromination of α-chloro-camphor both yielded a mixture of stereoisomeric $\alpha\alpha'$- and $\alpha'\alpha$-chlorobromocamphors, and then extended his work to the study of the nitro-camphors. In 1899, by chance, through measuring the optical activity of a solution of nitrocamphor in the morning, and then leaving the solution in the polarimeter tube for a confirmatory reading after lunch, he noticed in the camphor series the phenomenon of change of rotatory power with time, an effect which had previously been encountered only with aqueous solutions of sugars. Lowry described this phenomenon as *mutarotation*, and this term has been in general use ever since.

Another happy accident led to his discovery of the mechanism of this phenomenon. When recovering *d*-nitrocamphor (I) from its


(I.) *d*-Nitrocamphor.


(II.) *l*-*aci*Nitrocamphor.


(III.) *l*-Anhydride.

solutions in benzene, he happened to leave a solution to evaporate on the water-bath, and, by over-heating the solid, obtained an anhydride (III) which was evidently derived from an isomeric, lævo-rotatory, hydroxylic form of nitrocamphor (II), of which only salts are known.

The mutarotation was thus ascribable to the conversion of the group $CH{-}NO_2$ to the *aci*-form, $C{=}NO{-}O{-}H$, and this change, since it occurred in solvents such as benzene and chloroform, could not be explained as a reversible hydration and dehydration process, such as had been suggested for the mutarotation of glucose. In 1908, moreover, Lowry was able to show that the arrest of the mutarotation of nitrocamphor in chloroform was due to the development, through oxidation, of a little carbonyl chloride, which completely eliminated from the solution traces of nitrogenous bases, such as ammonia. Organic bases were then shown to be catalytically active in concentrations as low as 1 in 10^7, and by their complete removal the mutarotation of tetramethyl glucose, as well as that of nitrocamphor, could be arrested in many solvents, such as ether, benzene, and even ethyl acetate, provided that silica vessels were used.

This discovery of the catalytic activity of amines led Lowry, in 1923, to the conclusion that the currently accepted theory that catalyses by acids and bases were due respectively to hydrogen and hydroxyl ions was inadequate, and that acids and bases should be regarded in more general terms as proton-acceptor and proton-donator molecules. Thus :—

$$A{-}H + B = A^- + \overset{+}{B}{-}H$$

This "*Generalised Theory of Acidity and Basicity*", which in its essentials can be traced back to the contemporary writings of G. N. Lewis, was put forward quite independently a few months later by the Danish physical chemist J. N. Brönsted, who developed the subject much more fully in precise mathematical terms. Though it is to the later work of Brönsted and his school that the credit must be given for the subsequent development of the modern quantitative theory of acid–base catalysis, Lowry and his students in Cambridge were undoubtedly the first experimental workers to demonstrate that tautomeric changes involving the migration of hydrogen were not intramolecular, but involved reactions with solvent (or dissolved catalyst) molecules having *both* acidic and basic character. Thus, in 1927 they showed that the mutarotation of tetramethyl glucose

could be arrested both in dry cresol, which can function only as an acid, and in dry pyridine, which can function only as a base, but proceeded too rapidly for convenient measurement in mixtures of these two anhydrous solvents. The tautomeric change involved, termed by Lowry a *prototropic change*, thus comprised both hydrogen-ion removal by the basic catalyst and hydrogen-ion acceptance from the acidic catalyst :

$$\text{(i)}\quad B + H\text{–}S \longrightarrow (B\text{–}H)^+ + S^-$$
$$\text{(ii)}\quad S^- + H\text{–}A \longrightarrow S\text{–}H + A^-$$

where H–S and S–H represent the two tautomers concerned.

As Lowry pointed out, these reactions, which can be either simultaneous or consecutive, involve the transference of a valency electron through the interior of the anion S^-, to neutralise the charge of the proton which is transferred through the solvent. Lowry described the initial and final forms of the anion S^- as "*electromers*", since they differed only in the relative positions of their valency electrons, and came very closely indeed to the modern view—*viz.*, that the electromeric ions are but the separate, hypothetical, canonical states of one single *mesomeric ion* which is, in reality, a resonance hybrid of the two structures, for he pointed out that merely by the conversion of a double covalence to a "*semi-polar bond*" there could be produced one common structure for the "completely activated ion" of any tautomer : *e.g.* :

$$\mathrm{O{=}\underset{\displaystyle Me}{C}{-}\bar{C}H{-}CO_2Et} \qquad \mathrm{\bar{O}{-}\underset{\displaystyle Me}{\overset{+}{C}}{-}\bar{C}H{-}CO_2Et} \qquad \mathrm{\bar{O}{-}\underset{\displaystyle Me}{C}{=}CH{-}CO_2Et}$$

Keto-ion. Common activated ion. Enol ion.

Similarly, he pointed out that nitriles and *iso*nitriles are derived from a common cyanide anion.

$$\mathrm{R{-}C{\equiv}N\!:} \qquad \mathrm{(:C{\equiv}N:)^-} \qquad \mathrm{:\bar{C}{\equiv}\overset{+}{N}{-}R}$$

Nitrile. Cyanide anion. *iso*Nitrile.

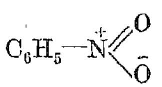
The special rôle of water, as a solvent which could both provide and accept protons, $HO\text{–}H + H_2O \rightleftarrows (HO)^- + (H_3O)^+$, was pointed out very clearly by Lowry as early as 1923, and the significance of the solvent chosen for effecting organic reactions was made evident in terms of an electrolytic theory of chemical change which can clearly be traced back to views held by H. E. Armstrong. Lowry pointed out too that prototropy was but one particular case of *ionotropy*, and, in a detailed review of this subject delivered at the Second Solvay

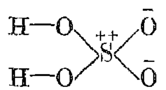
Conference in 1925, gave examples both of *anionotropic changes* involving groups such as hydroxyl, and of molecular rearrangements in which ionic migrations of hydrocarbon radicals were involved. Whilst later studies of prototropic changes in heavy water have fully substantiated his view that this type of isomeric change always involves an exchange of hydrogen ion between the tautomeric molecule and the (acid + base) catalyst system, it has now become evident that many of the more complicated ionotropic changes occur intra-molecularly, though the process can always be represented by a similar electrolytic circuit and is usually promoted by an acidic or basic catalyst.

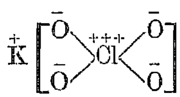
Throughout this period (1920—30) of his active work at Cambridge, Lowry laid great stress upon the idea of polar activation as a pre-requisite for chemical change. He emphasised the significance of the earlier work of Lapworth in this field, and did much to stimulate R. G. W. Norrish, and later Gwyn Williams, to follow up in his Department the experimental evidence for the polar mechanism for the surface-catalysed additions of halogen molecules to ethylene. This he represented as an ionic activation and recombination process, involving halogen ions and an activated "semi-polar" form of the ethylenic bond.

$$\begin{matrix} Br \\ | \\ Br \end{matrix} + \begin{matrix} CH_2 \\ \| \\ CH_2 \end{matrix} \longrightarrow \begin{matrix} Br^+ \\ Br^- \end{matrix} \quad \begin{matrix} {}^-CH_2 \\ | \\ {}^+CH_2 \end{matrix} \longrightarrow \begin{matrix} Br—CH_2 \\ | \\ Br—CH_2 \end{matrix}$$

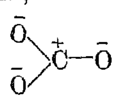
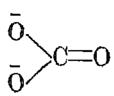
Typically, too, he extended this theory in other directions, and promptly revised his own text-books so as to write both organic and inorganic molecules with semi-polar bonds, and thus to emphasise the significance of the "octet rule" for molecular stability. He introduced formulæ such as:


Nitrobenzene.


Sulphuric acid.

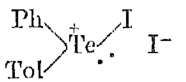
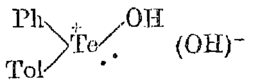

Potassium perchlorate.

and stressed the importance of *X*-ray measurements which showed that crystals of carbonates, nitrates, sulphates, etc., had spatially symmetrical anions,

e.g.  not 

Again, in the field of organic chemistry he emphasised the practical point that addition of polar groups (CN^-, SO_3Na^-, etc.) to sulphoxides

and sulphones does not occur, as might be expected of the double-bonded structure $>S{=}O$, because the electro-positive sulphur atom in this group (which he wrote as $>\overset{+}{S}-\overset{-}{O}$), unlike the carbon atom in the "activated" $>\overset{+}{C}-\overset{-}{O}$ form of the carbonyl group, has already completed its electron octet, and so has but little tendency to gain still more valency electrons. He claimed the discovery of the optical activity of the sulphinic esters by Kenyon and Phillips as being conclusive evidence in favour of the semi-polar structure of the sulphoxide group, and extended his "studies of valency" experimentally by syntheses of optically active telluronium salts, such as phenyl-*p*-tolyltelluronium di-iodide and phenyl-*p*-tolyltelluronium dihydroxide:

which, however, racemise very rapidly.

Only quite recently has it become clear that in this strong advocacy of the octet theory Lowry's views were too extreme, since heavy elements of Groups V—VIII, such as sulphur or arsenic, can, and frequently do, increase their valency shells beyond the octet, forming stable compounds which are resonance hybrids of the double covalency and the semi-polar states. The same can be said, too, of Lowry's complete ionisation theory for explaining the mechanisms of organic reactions, for since his death it has been established that many, but by no means all, displacement reactions do not involve the complete ionisation of the organic compound concerned, but proceed bimolecularly through the formation of a transition complex. Nevertheless Lowry's contributions to theories of the mechanisms of organic reactions were, in their time, invaluable, for, though more extreme than those of his British and American contemporaries, they were pictorially more satisfying, and so more easily comprehensible to the average reader, who was thus able to realise the great significance of the electronic theory of valency and become able to use it as a mental tool in the solutions of his own problems. The striking result of clear teaching of this type may be seen to-day, for the European continent, where the electronic concepts had no advocate comparable to Lowry, is already noticeably lacking in its output of new achievements in theoretical and physico-organic chemistry.

His Work: II. Optical Rotatory Dispersion.

From the death of Biot in 1862 up to the time when Lowry's investigations of mutarotation were being carried out, little work had been done on the *dispersion* of optical rotatory power. It was perhaps Lowry's most important contribution to physical science that he realised that little progress in this field could be made unless values of rotatory power were measured over the widest possible range of wave-lengths, instead of for a single arbitrarily selected point on a dispersion curve. So much had this been neglected, that when Drude wished to test his mathematical theory of rotatory power (1907) the only data available were some rather inaccurate measurements with quartz. In 1913 Lowry was able to show that the optical rotations of ten simple alcohols could be expressed by *one term* of Drude's equation: $\alpha = \Sigma \frac{k}{\lambda^2 - \lambda_0{}^2}$. A year later he showed that *two terms of opposite sign* would completely represent the "anomalous" rotatory dispersion of ethyl tartrate, thus demonstrating quantitatively that "anomalous" rotatory dispersion has its origin in the superposition of two "partial rotations" of opposite sign and of unequal dispersions contributed by separate absorbing centres in the molecule.

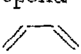
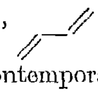
Drude's equation is only applicable to transparent media, for which the limits of its validity coincide with the conditions under which maximum experimental accuracy can be obtained. Lowry reached these limits in the case of quartz, where his very accurate measurements with a column nearly half a metre in length, giving a rotation of 12,678·96° for the Hg 5461 line, extended down to 2263 A. (with a rotation of over 100,000°) in one direction, and to 3·2 μ in the other, the latter wave-length lying beyond the first infra-red absorption band. Over this entire range, the rotation, for about 1000 wave-lengths, could be expressed with the greatest precision by a Drude equation containing two terms of opposite sign together with a small constant.

The validity of Drude's equation having thus been established, Lowry proceeded to rigid definitions of "normal" and "anomalous" rotatory dispersion—namely, where the rotation α, $d\alpha/d\lambda$ and $d^2\alpha/d\lambda^2$ all pass through zero values respectively. Applying the equation to camphor, it was discovered that most of the optical activity of this compound was associated with the ketonic absorption band at about 2700 A., and not with the electrons of the carbon

atoms, whose absorption frequencies lie at much shorter wave-lengths. To explain this result, Lowry and E. E. Walker, in 1924, put forward the conception of "induced dissymmetry", in which the ketonic radical was pictured as becoming dissymmetric under the influence of the remainder of the dissymmetric molecule. This rather revolutionary concept has found modern expression and complete justification in the "one electron theory" of rotatory power developed by H. Eyring and his collaborators. The resulting importance of making measurements of rotatory power inside regions of the spectrum covered by absorption bands, instead of in the regions of complete transparency, led Lowry to devote his attention between 1930 and 1936 to this far more difficult problem, in which he achieved considerable success. He modified equations developed by W. Kuhn on the basis of a simplified model and applied them to the analysis of his experimental data. Perhaps the most spectacular result was the demonstration that the apparent simplicity of the rotatory dispersions of two aldehydic sugars, tetra-acetyl μ-arabinose and penta-acetyl μ-fructose, which had been prepared by Wolfrom, was due to the fact that the "partial rotations" contributed by the asymmetric carbon atoms almost exactly cancelled one another, leaving the simple contribution of the aldehydic radical alone.

Lowry thus became keenly interested in the more physical aspects of the problem of the origin of optical rotatory power, and he was instrumental in obtaining a wide publicity for two quite different theories put forward by younger workers, W. Kuhn and S. F. Boys, between 1930 and 1935. When Max Born settled in Cambridge in 1934, Lowry provoked him—by a remark in the Presidential Address to Section B of the British Association, that "the real theory of optical rotatory power may be found by the mathematician, but is concealed from the chemist, in the papers of Born"—to restate his earlier mathematical theory (1915). This had originally been applied only to optically active crystals, but was now re-interpreted in 1934 in parameters accessible to chemists, and applied with immediate qualitative and quantitative success to the spatially dissymmetric *spiro*-compounds which had just been resolved by Sir William Pope. At the time of his death Lowry was busily applying these newer electronic theories to the problem of the changes in the rotatory powers of amines which result when they are ionised or when the charges on the amino-nitrogen atoms are neutralised.

While Lowry's main optical work was connected with optical

rotatory power, he did not neglect parallel lines of research. Thus, his earlier tests of Drude's equation were combined with corresponding measurements of magneto-rotatory dispersion. He also began a series of researches on the refractive dispersion of organic compounds with the general object of providing a sound experimental basis for the development of physical theories. In particular, he tried to elucidate the origin of the apparently anomalous refractivities ("optical exaltation") associated with conjugated systems. The conclusion which he reached, that the refractivity would depend on whether the double bonds were arranged in a "*cis*"  or a "*trans*"  orientation, was at first described as "speculative" by contemporaries, but subsequently found its place in Mulliken's comprehensive mathematical theory of the phenomenon. Lowry always sought to discover possible relationships between chemical behaviour and the various optical phenomena which he could observe. It became a matter of routine for the absorption spectrum of any compound with which he or his pupils were working to be recorded. Precise optical measurements were always important to him, not only for their own sake, but as a powerful weapon of attack on other problems.

HIS WORK: III. INORGANIC CHEMISTRY.

Lowry's investigations in the field of inorganic chemistry can be regarded as an outcome of his scientific services during the First World War of 1914—18, and several of them proved of value during the Second World War of 1939—45.

As Director of Shell Filling he was largely concerned with the production and use of amatol mixtures, and the difficulties which arose owing to the polymorphism of ammonium nitrate. He determined the four transition temperatures between the five solid forms of this salt and ascertained the form of the velocity curve for the change of state; he also plotted the equilibrium diagram between ammonium nitrate and water.

On his arrival at Cambridge he took up the study of the chlorides of sulphur, which had become of importance in connection with the manufacture of "mustard gas" by the processes developed by W. J. Pope and C. S. Gibson. By a series of freezing-point determinations, he was able to prove the existence of the red sulphur dichloride, SCl_2, in solution and to obtain it as a crystalline solid at low temperatures. He measured the proportion of sulphur dichloride present

in liquid sulphur–chlorine systems by means of its absorption of light of wave-lengths 5200 and 5400 A., to which sulphur monochloride and chlorine are transparent, introducing here a technique which has been developed in much greater detail by later workers. Lowry also obtained trisulphur tetrachloride, S_3Cl_4, and sulphur tetrachloride, SCl_4, the latter being an almost colourless crystalline solid which dissociates so rapidly that no evidence could be obtained of its existence in the liquid phase. He found that sulphur tetrachloride is anomalous in having a higher dielectric constant in the solid state than when fused, a behaviour which he interpreted by the suggestion that the following change in molecular structure occurs on fusion :

$$\text{(Solid)} \quad (SCl_3)^+Cl^- \longrightarrow SCl_2 + Cl_2 \quad \text{(Liquid)}$$

Lowry noted that phosphorus pentachloride similarly has a higher dielectric constant in the solid than in the liquid state; this he also attributed to a change in molecular structure, although there can be no doubt of the existence of the PCl_5 molecule in both the liquid and the gaseous phase.

The investigations of the sulphur chlorides were complicated by the occurrence of a number of dissociation reactions which proceed with different velocities, and are influenced by the presence of catalysts, such as ferric chloride, but Lowry was able to confirm his conclusions by measurements of dielectric constants and parachors. It was found that sulphur dichloride, in glass, is usually dissociated into the monochloride and chlorine at room temperature, but that this dissociation can be "arrested" so completely by the addition of a small proportion of phosphorus pentachloride that it is possible to purify sulphur dichloride by fractional distillation.

During the last few years of his life, Lowry was engaged on the experimental study of the binary systems N_2O_3–H_2O and N_2O_4–H_2O, with a view to completing the triangular phase diagram for the ternary system H_2O–N_2O_3–N_2O_5 which is of such obvious importance in connection with nitration and the manufacture of stable explosives. In the course of this work it was noticed that, when nitrogen peroxide was passed into ozonised oxygen, the gaseous mixture ignited below 100° showing a deep blue wave-front. This blue gas was probably NO_3.

Looking back ten years after his death, it is possible to see Lowry as a man and a scientist in a truer perspective. He was undoubtedly

a great teacher and a meticulously exact experimenter who had personal interests extending far beyond his scientific research. His influence will persist for many years still through his books. His contributions to science have been grouped in three separate fields. Only in one of them—mutarotation—were his researches complete : but the other problems had reached stages when ultimate success was already assured. He died in harness, his unduly early death having been accelerated by the intensity with which he had lived. Many people, some in most unexpected walks of life, remember him with gratitude as a real friend, while scientists will never forget him for his distinguished work, which entitles him to a permanent place in the first rank of British Chemists.

[*Reproduced by permission of the Royal Society.*

G Barger

GEORGE BARGER

1878—1939

By the sudden death on January 6th, 1939, at the age of sixty years, of Professor George Barger this country lost one of its ablest workers in organic chemistry.

George Barger was born in Manchester in 1878, his father, Gerrit Barger, being a Dutch engineer and his mother English. During his childhood the family lived in Utrecht, where he attended school until he was sixteen years old. He then chose to complete his education in England and proceeded to University College, London, with a scholarship which he had obtained on the University Matriculation Examination. After commencing his studies for the London B.Sc. at University College, he won a scholarship to King's College, Cambridge, which he subsequently took up.

Barger's wide interests in later life were doubtless due in part to the fact that his early scientific training was on a broader basis than that of many organic chemists. As an undergraduate at Cambridge his interests were divided between Botany and Chemistry, and he was actually placed in the first class of Part II of the Natural Sciences Tripos in both Botany and Chemistry on the last occasion on which it was possible to offer two subjects for this examination. Although he never did any botanical research, Barger retained his interest in the plant throughout his life.

The first academic appointment which Barger held was a demonstratorship under the late Professor Leo Errera in the Department of Botany of the University of Brussels; here he spent two years, and during this time he worked out the micro-method of molecular weight determination which bears his name. The method has not found very wide application, having been replaced by others which are more accurate and convenient; nevertheless, the ingenious application of the principle of isothermal distillation which it embodied showed a marked freshness of mind and an early appreciation of the importance of micro-methods in the study of biological chemistry.

On his return from Brussels in 1903, Barger entered the Wellcome

Physiological Research Laboratories as chemist. Although he only took this post after considerable hesitation, the appointment was of decisive importance for his future development; not only were the six years which he spent in the Wellcome Laboratories some of the most fruitful of his life, but the contacts which he made there with biological workers, and particularly in his long collaboration with Dr. (now Sir Henry) Dale, gave him a broadness of outlook which influenced the whole of his later work.

Barger remained in the Wellcome Laboratories until 1909, when he left to become Head of the Department of Chemistry at Goldsmiths' College in the University of London; in 1913 he was appointed to the Chair of Chemistry at the Royal Holloway College.

He had not held this appointment long before he joined the research staff of the recently formed Medical Research Committee, and he continued in this post throughout the First World War; during this period his energies, like those of most other chemists, were mainly diverted to work of immediate national importance, although even in these circumstances he published several papers of scientific interest.

In 1919 Barger was appointed to the newly constituted Chair of Chemistry in Relation to Medicine at Edinburgh, and in this position he found himself called upon to spend a much greater proportion of his time than had formerly been the case in duties of teaching and administration. The conditions at the time of his appointment were anything but favourable. The medical school at Edinburgh had received an enormous influx of new students, a large proportion of whom had little prospect of completing their course; some attempt had to be made, however, to teach them elementary chemistry and the present writer has a vivid recollection of assisting in the attempt to demonstrate to classes which had to be held in quadruplicate owing to insufficient accommodation. The shortage of accommodation, both for teaching and for research, persisted, indeed, for some years, until the Department of Chemistry moved out to its new quarters in the King's Buildings at Liberton. In these circumstances it is not surprising that Barger's output of research should have suffered for a time, but he never allowed his interest to slacken, and even at the busiest periods he took every opportunity to snatch a few moments in the laboratory.

Barger remained at Edinburgh until, a little more than a year before his death, he was appointed to the Regius Professorship of Chemistry in the University of Glasgow. This important appoint-

ment was a fitting recognition of his distinguished position in the profession of Chemistry in this country. It brought with it heavy burdens, but he threw himself into the task of reorganising a large department with a freshness and enthusiasm which surprised even his friends. It is sad to think that this task, with which he had already made so much progress, should have had to be left unfinished.

Barger's scientific work falls naturally into two main divisions, his studies of alkaloids and his investigations of simpler nitrogenous compounds of biological interest.

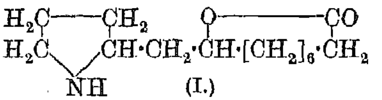
One of the first investigations which he undertook in the Wellcome Laboratories was a study of the alkaloids of ergot; the work which he did on this subject was the basis of his first publication in the field of alkaloid chemistry, and since this field remained a major interest throughout his whole life, occupying indeed the greater part of his attention in recent years, it has seemed better to give first a continuous account of his main contributions to the chemistry of alkaloids rather than to attempt to present the whole of his work in strictly chronological sequence.

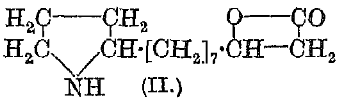
Ergotoxine.—At the time when Barger and F. H. Carr took up the study of ergot considerable confusion existed concerning the physiologically active substance produced by this fungus. The only crystalline alkaloid known to be extractable from ergot was the ergotinine which had been discovered by Tanret, and this was physiologically inactive. Barger and Carr (*J.*, 1907, **91**, 307) described the isolation of a new alkaloid, $C_{35}H_{41}O_6N_5$, the salts of which could be obtained crystalline, and which showed a high degree of physiological activity. They showed moreover that the new alkaloid, which they named ergotoxine, was convertible into ergotinine by treatment with acetic anhydride, the change being interpreted as due to the loss of the elements of water. This observation was the first example of what has since turned out to be a general characteristic of all ergot alkaloids, namely, that they occur in isomeric pairs, the members of which are interconvertible by simple means with large changes in specific rotation and physiological action.

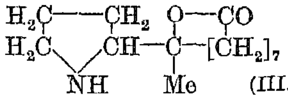
With Ewins (*J.*, 1910, **97**, 284) Barger later studied the degradation of ergotoxine and observed the production of *iso*butyrylformamide on pyrolysis of the alkaloid. The significance of this observation was not appreciated until, many years later, the brilliant work of Jacobs (following on the observations of Smith and Timmis) revealed the general nature of the ergot alkaloids as compounds of lysergic

acid with amino-acids or substances derived therefrom; it then became clear that *iso*butyrylformamide must represent a link between the components in ergotoxine.

Carpaine.—The next alkaloid to attract Barger's attention was carpaine. He observed (*J.*, 1910, **97**, 466) that this compound, $C_{14}H_{25}O_2N$, could be hydrolysed to a substance, $C_{14}H_{27}O_3N$, which he named carpamic acid, thus indicating the presence of a lactone group in carpaine; carpamic acid, on oxidation, gave a dicarboxylic acid, $C_8H_{14}O_4$, at that time supposed to be $\alpha\delta$-dimethyladipic acid. More than twenty years later he resumed the study of carpaine and was then able (Barger, Girardet, and Robinson, *Helv. Chim. Acta*, 1933, **16**, 90) to prove the presence in it of a pyrrolidine ring, since dehydrogenation under mild conditions with selenium yielded a


(I.)

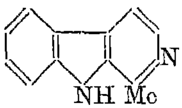

(II.)


(III.)

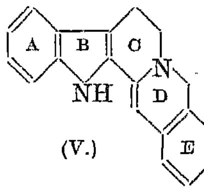
pyrrole derivative, $C_{14}H_{21}O_2N$, which could be re-hydrogenated to a compound isomeric with the original alkaloid. Further investigation of the oxidation products of carpamic acid revealed the presence among them of azelaic and suberic acids, the latter being the acid $C_8H_{14}O_4$ already mentioned. The formation of azelaic acid proved the existence of a continuous chain of at least 9 carbon atoms in carpamic acid, and the facts available at this stage led to the suggestion of the two alternative formulæ (I) and (II), of which (I) with the large lactone ring was favoured. Later (Barger, Robinson, and Work, *J.*, 1937, 711) came the recognition of the presence of a *C*-methyl group; this, together with the consideration that carpamic acid is a tertiary alcohol, led to formula (III), which is at present accepted as representing the structure of carpaine.

Yohimbine.—In 1915 (Barger and Field, *J.*, 1915, **107**, 1025) Barger made a preliminary study of the degradation of yohimbine, in the course of which he observed the formation of indole derivatives during alkaline fusion of yohimbic acid. Many years later, with Scholz (*J.*, 1933, 614), he identified among these degradation products 3-ethylindole, indole-2-carboxylic acid and, most significantly, harman (IV).

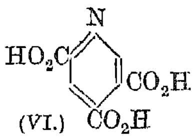
In the intervening years much information had been forthcoming from the work of others concerning the structure of yohimbine, and in 1933 Barger and Scholz (*Helv. Chim. Acta*, 1933, **16**, 1343) published a valuable paper in which cogent reasons are given for regarding the structure of yobyrine (a selenium dehydrogenation product of yohimbine obtained by Wibaut) as being represented by (V). Yobyrine is regarded in turn as representing the essential skeleton



(IV.)



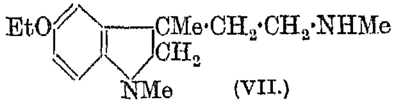
(V.)



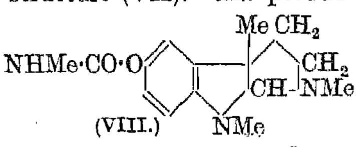
(VI.)

of yohimbine, in which ring E is fully hydrogenated. Two major arguments for the proposed structure rest on observations for which Barger was himself responsible, namely, the isolation of harman, which fixes the arrangement of rings A, B, and C, and the detection of berberonic acid (VI) among the oxidation products, which must represent ring D.

Physostigmine (Eserine).—With his pupil Stedman (*J.*, 1923, **123**, 758) Barger published a detailed study of the complicated series of products obtained in the exhaustive methylation of eseroline (the phenolic compound obtained by removal of the methylcarbamido-group from eserine), and of eserethole (eseroline ethyl ether). In the course of this it was recognised that eseretholemethine, produced by the action of alkali on eserethole methiodide, was a ψ-base, reconvertible into eserethole methiodide by treatment with hydriodic acid. It was also confirmed that the final Hofmann degradation product of eserethole, physostigmol ethyl ether, was an indole derivative. The synthesis of the latter compound by Stedman (*J.*, 1924, **125**, 1373) proved physostigmol to be 5-hydroxy-1 : 3-dimethylindole and thus fixed the orientation of the indole portion of the eserine molecule. The remainder of the structure was elucidated by Stedman and Barger (*J.*, 1925, **127**, 247), who showed that reduction of eserethole led to the formation of a secondary base which they regarded as having the structure (VII). The pseudo-

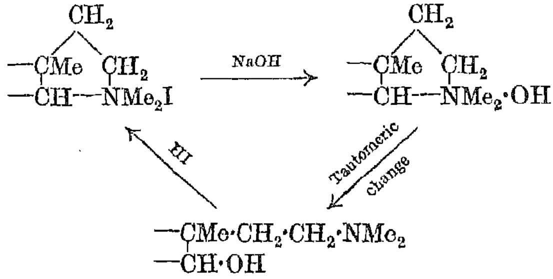


(VII.)



(VIII.)

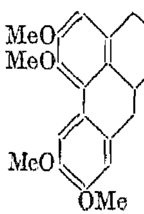
basic character of eseretholemethine already referred to was explained by supposing it to be an α-hydroxyindoline formed as follows :



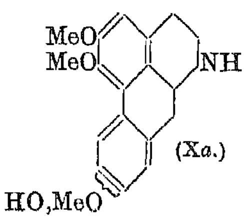
Confirmation of this hypothesis by the formation of indolinones on oxidation and considerations of the probable biogenesis of the alkaloid led the authors to propose (VIII) as the formula of eserine. As is well known, this formula has since been shown to be correct by the synthetic studies of other workers.

The investigation of eserine is of importance not only in itself but as the foundation of the later well-known work of Stedman on the physiological action of simpler but analogous urethanes, among which at least one substance (the prostigmine prepared by Aeschlimann) has proved to be of great pharmacological and therapeutic value.

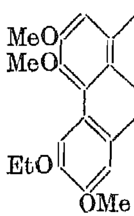
Aporphine Alkaloids.—During the years 1928 to 1933, Barger made a number of investigations of a group of related alkaloids, namely, laurotetanine from *Litsea citrata*, Bl., and the pukateine–laureline–lauropukine group from *Laurelia Novae Zealandiae*. The first of these to be studied was laurotetanine. This alkaloid was already known to be closely related to glaucine (X), from which it differs only in having no *N*-methyl group and one less *O*-methyl. Earlier work by Gorter had appeared to show that *ON*-dimethyllaurotetanine was not identical with glaucine; Barger and Silberschmidt (*J.*, 1928, 2919), however, by subjecting laurotetanine and



(X.)

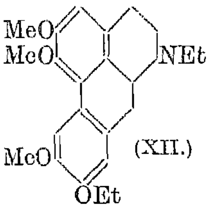


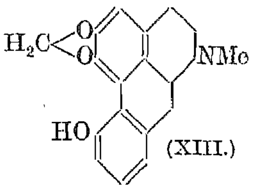
(X*a*.)

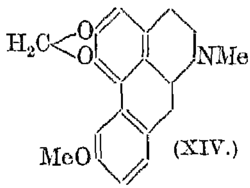


(XI.)

glaucine in turn to Hofmann degradation, obtained identical series of (phenanthrene) derivatives; it thus followed that laurotetanine and glaucine had the same fundamental structure and the former could be formulated as (X*a*). The doubt as to the relative positions of the hydroxyl and methoxyl groups was settled by Barger, Eisenbrand, Eisenbrand, and Schlittler (Ber., 1933, **66**, 450) in an indirect manner. The compounds (XI) and (XII) were synthesised and the products obtained from them by Hofmann degradation were compared with those similarly obtained from *ON*-diethyl-laurotetanine. By this means ethylated laurotetanine was proved to be identical with (XII), whence the constitution of the alkaloid follows.


(XII.)


(XIII.)


(XIV.)

Similarly complete information was obtained regarding pukateine (XIII) and laureline (XIV), the formulæ being proposed on the basis of Hofmann degradation and oxidation experiments by Barger and Girardet (*Helv. Chim. Acta*, 1931, **14**, 481) and subsequently confirmed by the synthesis of *O*-methylpukateine (Barger and Schlittler, *ibid.*, 1932, **15**, 381) and of laureline itself (Schlittler, *ibid.*, 1932, **15**, 394).

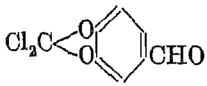
During the past few years Barger had been engaged with J. J. Blackie on a systematic study of the *Senecio* alkaloids, and at the time of his death one of his main interests lay in work which he was doing on the difficult problem of the constitution of calycanthine.

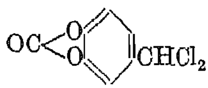
Important as were Barger's contributions to alkaloid chemistry he will perhaps be remembered even more for his work in the field of what he himself called the "simpler natural bases". This work was largely done while he was in the Wellcome Laboratories.

At the time when he took up his post there the active principle of the suprarenal gland, adrenaline, had recently been isolated and its constitution had been determined. The chemistry of this substance naturally attracted much attention and Barger, in collaboration with H. A. D. Jowett took up the attempt to synthesise it. In this he was not completely successful, but his efforts were embodied in

an interesting paper (Barger and Jowett, *J.*, 1905, **87**, 967) on the synthesis of compounds closely related to adrenaline.

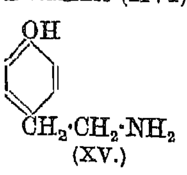
These experiments led first to an observation of some chemical interest. An obvious starting material for the synthesis of adrenaline would be piperonal, provided that the methylenedioxy-group could be converted into the corresponding catechol. In studying the possibilities in this direction, Barger (*J.*, 1908, **93**, 563) examined the action of phosphorus pentachloride and thionyl chloride on piperonal; the former reagent was already known to yield a tetrachloro-derivative which lost two chlorine atoms on treatment with water to give what was supposed to be the compound (A). Barger

(A.) 

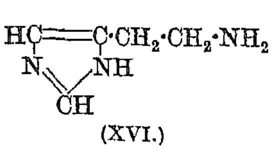
 (B.)

found, however, that an identical dichloro-compound could be prepared from piperonal directly by the action of thionyl chloride and that it actually had the structure of a cyclic carbonate (B). This reaction was subsequently shown by Barger to be generally applicable to methylenedioxybenzenes.

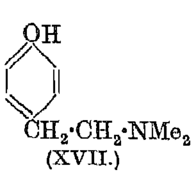
The much more important outcome of the experiments towards the synthesis of adrenaline was, however, the interest which they aroused in Barger's mind in the physiological action of relatively simple basic compounds. This phase of his work, throughout which he collaborated with Dale, began with a return to the study of ergot. The isolation of ergotoxine had done something to explain the physiological activity of extracts of ergot, but still left much unaccounted for; Barger first showed (*J.*, 1909, **95**, 1123) that a part of the unidentified activity was due to the presence of tyramine (XV), which compound he also synthesised; later (Barger and Dale, *J.*, 1910, **97**, 2592), he isolated the still more active substance histamine (XVI) from the same source.



(XV.)



(XVI.)



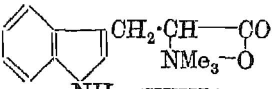
(XVII.)

In 1911 (Barger and Dale, *J. Physiol.*, 1911, **41**, 499) Barger demonstrated for the first time the occurrence of histamine in an animal tissue (gut); later developments in physiology and pathology have given this observation an importance which could not at the

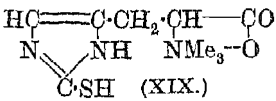
time be appreciated. In connection with this it may be mentioned that in continuation of Barger's work his pupil Ewins was subsequently able to isolate acetylcholine from a particular ergot extract, and this compound also has since proved to have a profound physiological importance. The physiological implications of one aspect of this work as they were then apparent were treated in the classical paper of Barger and Dale (*J. Physiol.*, 1911, **41**, 19) in which the general conception of sympathomimetic amines was developed.

During this period Barger published several other papers dealing with compounds allied to those under discussion; among these may be mentioned the syntheses of hordenine (XVII), the alkaloid of barley (*J.*, 1909, **95**, 2193), and of hypaphorine (XVIII), the betaine of tryptophan (Van Romburgh and Barger, *J.*, 1911, **99**, 2068), which occurs in the seeds of *Erythrina hypaphorus*.

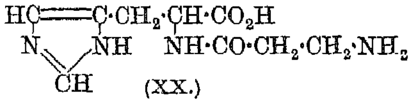
With Ewins (*J.*, 1911, **99**, 2336) he showed that ergothioneine, a sulphur-containing substance which had been isolated by Tanret from ergot, was the betaine of mercaptohistidine (XIX), and with



(XVIII.)



(XIX.)



(XX.)

Tutin (*Biochem. J.*, 1918, **12**, 403) he was able to prove by synthesis that the muscle extractive carnosine had the structure of β-alanylhistidine (XX).

Barger made another contribution in the field of amino-acid chemistry when he proved the constitution of the amino-acid methionine, $CH_3 \cdot S \cdot CH_2 \cdot CH_2 \cdot CH(NH_2) \cdot CO_2H$, which had been discovered by Mueller in 1923. He synthesised this compound first in 1928 (Barger and Coyne, *Biochem. J.*, 1928, **22**, 1417) and later by an improved method (Barger and Weichselbaum, *ibid.*, 1931, **25**, 997).

Reference should be made to one other piece of work which Barger did, not because it led to any results of importance, but because at one time it exercised a peculiar fascination over his mind. At the time when he was in Brussels he studied a glucoside, saponarin (actually the subject of his first published paper); this substance had the unusual property of giving a blue compound with iodine

similar to that given by starch. The observation attracted Barger's interest and he returned to the subject on several occasions in later years; he found that the property of forming such blue complexes with iodine was generally associated with the γ-pyrone group, and he published several papers (Barger and Field, *J.*, 1912, **101**, 1394; Barger and Starling, *J.*, 1915, **107**, 411; Barger and Eaton, *J.*, 1924, **125**, 2407) dealing with the theory of the reaction and with constitutional factors affecting it.

Finally, mention must be made of two researches in which Barger played a less direct but nevertheless important part, namely, the work of the present writer on thyroxine and that of A. R. Todd on vitamin B_1 (aneurin). At the time when the writer started to work on thyroxine he had already left Barger's laboratory several years. This did not, however, prevent consultation by correspondence, and the keenness of Barger's interest and the freedom with which he gave of his experience did much to further the progress of the work. Incidentally it is typical of Barger that, in spite of this, he so far belittled the value of his own contribution as only with difficulty to be persuaded to agree to joint publication of the final stage.

The recent distinguished work of A. R. Todd and his collaborators on the constitution and synthesis of aneurin was begun and largely carried through in Barger's laboratory in Edinburgh. In the early stages of this work, particularly, his contribution was of great value.

Apart from his original papers in scientific journals Barger published several books; in his monograph on "The Simpler Natural Bases", which appeared in 1914, he collected a large amount of chemical and physiological information which was otherwise not easily accessible. In 1930 he published "Some Applications of Organic Chemistry to Biology and Medicine", and in 1932 a text-book entitled "Organic Chemistry for Medical Students"; the book by which he will chiefly be remembered, however, is the monograph "Ergot and Ergotism", which appeared in 1931. The writing of this masterly book was a labour of love extending over many years; in it every aspect of the subject is treated with a sureness of touch and a scholarly finish which make the work a model of its kind.

Barger's work was recognised by many distinctions in this and other countries. He was elected a Fellow of King's College, Cambridge, in 1904. In 1919 he was admitted to the Fellowship of the Royal Society; he served on the Council in 1930—32, and a few weeks before his death he was awarded the Davy Medal. He was a member of the Council of the Chemical Society in 1913—17

and a Vice-President at the time of his death; in 1936 he was Longstaff Medallist. In 1934 he received the Hanbury Medal from the Pharmaceutical Society. In 1928 he held the Baker visiting Professorship of Chemistry at Cornell University, and during the same year he delivered the Dohme lectures at the Johns Hopkins University, Baltimore. The British Association elected him President of Section B (Chemistry) for their meeting in South Africa in 1929. He received honorary degrees from the Universities of Liverpool, Padua, Heidelberg, Michigan, Lausanne, and Utrecht, and he was an honorary or corresponding member of many foreign academies.

Barger's bilingual upbringing was the foundation of the exceptional linguistic capacity which he developed in later life and which reached its climax when he was able to address the International Physiological Congress in Moscow in 1935 in eight different tongues. This facility for acquiring foreign languages was combined with a great enthusiasm for travel, and enabled him to make many contacts with colleagues in other countries. These contacts, which developed in several cases into close friendships, were of great value not only to himself but to the cause of mutual understanding between scientific workers which he had so much at heart. He was truly recognised as an international figure in Science, and the many honours which he received from foreign Universities and Academies indicate the high regard in which he was held by his colleagues abroad; this regard was shown in another way, however, which meant even more to him, namely, by the constant flow of foreign students who passed through his laboratory.

Barger's death was felt not only as a loss to Science but as a personal grief to his many friends. Those who were but slightly acquainted with him may not have realised to what an extent he possessed the gift of true friendship. He was not the most patient of men and his manner at times made him seem far less patient than he really was, so that the first stages of acquaintanceship with him were the most difficult and there were even some who never succeeded in surmounting the initial barrier. Those who were admitted to his friendship, however, found it difficult to remember that any such barrier had ever existed; there can, indeed, have been few men who were willing to do so much in any way and at any time for their friends, or who were capable of showing so true a human sympathy.

To his pupils he gave without stint, both of his thought to their problems, and of his time in the laboratory to their practical diffi-

culties. At the same time he did all in his power to encourage independence of thought and was at pains never to dissuade a student from testing a new idea experimentally even though he might himself feel sure from his own experience that the reaction would not "go".

It was indeed this love for experiment which was the keynote of Barger's attitude towards his work; he was instinctively mistrustful of hypotheses which were allowed far to outrun experimental support and this habit of mind coloured his whole outlook. It caused him to have strong leanings towards a mechanistic philosophy, departure from which, as he said in a discussion on the nature of life at the meeting of the British Association in 1929, he could not but regard as treachery of Science.

He himself possessed a high degree of experimental skill and had been at particular pains to perfect himself in the technique of working with small amounts of material, long before such technique came to be generally regarded as a part of the equipment of an expert organic chemist. This capacity for the fine handling of small quantities was somewhat paradoxically combined with unsystematic not to say untidy, habits in ordinary laboratory work.

Barger remained always a fundamentally simple-minded man; completely honest and straight-forward in his outlook, he never hesitated to express his views on any subject on which he felt strongly. He had little patience with formality and little respect for conventions, although he would not willingly disregard conventions in such a manner as to offend others who might feel differently. It was inevitable that he should at times have irritated less outspoken people, and thus have made things more difficult for himself, but he was not easily deterred by the thought of such consequences if what he had to say was a matter of conviction. This essential sincerity made it impossible for him effectively to conceal his true feelings, even on those occasions when he judged that such concealment would facilitate the attainment of his object.

Essentially non-political in outlook, Barger was a man of liberal views with whom it was a ruling desire to break down all barriers, such as those of nationality, which interfere with the free intercourse of men of science; enough has already been said to indicate how great were his services in the pursuit of this idea, and in these times particularly the measure of success which he achieved remains an encouragement.

No account of Barger would be complete without reference to the

warm hospitality of himself and Mrs. Barger, not only to friends and colleagues, but to students who were working with him; for many who have passed through his laboratory the remembrance of this will be one of their happiest recollections.

Barger died as he would have wished while still in full activity; he left to his friends the memory of a beloved personality, and to his pupils an enduring inspiration.

Printed and Bound in Great Britain by
Richard Clay and Company, Ltd.,
Bungay, Suffolk.